

ORIGIN AND EVOLUTION OF PLANETARY ATMOSPHERES¹

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INTRODUCTION

Spacecraft and groundbased observations of the atmospheres of solar system objects have provided a definition of their present characteristics and have yielded clues about their past history. Table 1 presents a summary of our current knowledge of the atmospheric properties of all the planets, except Pluto, and several satellites. The masses of these atmospheres range from the very miniscule values for the Moon, Mercury, and Io, to the more substantial values for the Earth, Venus, Mars, and Titan, to the very large values for the giant planets, where the atmosphere constitutes a significant fraction of the total planetary mass. The compositions of these atmospheres encompass ones dominated by rare gases (the Moon and Mercury), ones containing highly oxidized compounds of carbon, nitrogen, and sulfur (the outer three terrestrial planets and Io), and ones with highly reduced gases (Titan and the giant planets). What factors account for this enormous diversity in properties?

There are reasons for thinking that in the past these atmospheres were quite different from their present state. For example, it is considered highly unlikely, if not impossible, for the chemical steps that led to the origin of life on the Earth to have occurred with the current, highly oxidized atmosphere. Rather, an early, somewhat reducing atmosphere needs to be postulated (Miller & Orgel 1974). In the case of Mars, certain

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Table 1 Properties of the atmospheres of solar system objects

Object	\bar{p}^a	g^a	P_s^a	T_s^a	Major gases ^a	Minor gases ^a	Aerosols ^a
Mercury	5.43	3.95×10^2	$\sim 2 \times 10^{-15}$	440	He(~ 0.98), H(~ 0.02) ^b	—	—
Venus	5.25	8.88×10^2	90	730 (~ 230)	CO ₂ (0.96), N ₂ (~ 0.035)	H ₂ O(20–5000), SO ₂ (~ 150), Ar(20–200), Ne(4–20), CO(50) ^c , HCl(0.4) ^c , HF(0.01) ^c	Sulfuric acid (~ 35)
Earth	5.52	9.78×10^2	1	288 (~ 255)	N ₂ (0.77), O ₂ (0.21), H ₂ O(~ 0.01), Ar(0.0093)	CO ₂ (315), Ne(18), He(5.2), Kr(1.1), Xe(0.087), CH ₄ (1.5), H ₂ (0.5), N ₂ O(0.3), CO(0.12), NH ₃ (0.01), NO ₂ (0.001), SO ₂ (0.0002), H ₂ S(0.0002), O ₃ (~ 0.4)	Water (~ 5) Sulfuric acid (~ 0.01 – 0.1) ^d Sulfate, sea salt Dust, organic (~ 0.1) ^d
Mars	3.96	3.73×10^2	0.007	218 (~ 212)	CO ₂ (0.95), N ₂ (0.027), Ar(0.016)	O ₂ (1300), CO(700), H ₂ O(~ 300), Ne(2.5), Kr(0.3), Xe(0.08), O ₃ (~ 0.1)	Water ice (~ 1) ^e Dust (~ 0.1 – 10) ^e CO ₂ ice (?) ^e
Moon	3.34	1.62×10^2	$\sim 2 \times 10^{-14}$	274 (129)	Ne(~ 0.4), Ar(~ 0.4), He(~ 0.2) H ₂ (~ 0.89), He(~ 0.11)	—	—
Jupiter	1.34	2.32×10^3	$\geq 100^f$			HD(20), CH ₄ (~ 2000), NH ₃ (~ 200), H ₂ O(1 ³), C ₂ H ₆ (~ 5) ^f , CO(0.002), GeH ₄ (0.0007), HCN(0.1), C ₂ H ₂ (~ 0.02) ^f , PH ₃ (0.4)	Stratospheric “smog” (~ 0.1) Ammonia ice (~ 1) Ammonium hydro- sulfide (~ 1) Water (~ 10)

Saturn	0.68	8.77×10^2	$\geq 100^f$	(97) $H_2(\sim 0.89)$, He(~ 0.11) $NH_3(\sim 200)$, $C_2H_6(\sim 2)^f$ $CH_4(\sim 3000)$	Same aerosol layers as for Jupiter
Uranus	1.55	9.46×10^2	$\geq 100^f$	(58) $H_2(\sim 0.89)$, He(~ 0.11) CH_4	Same aerosol layers as for Jupiter, but thinner smog layer plus possibly methane ice
Neptune	2.23	1.37×10^3	$\geq 100^f$	(56) $H_2(\sim 0.89)$, He(~ 0.11) CH_4	Same aerosol layers as for Jupiter, plus possibly methane ice
Titan	~ 1.4	$\sim 1.25 \times 10^2$	$2 \times 10^{-2} \rightarrow \sim 1$	~ 85 $CH_4(0.1-1)$ $C_2H_6(\sim 2)$	Stratospheric "smog" (~ 10)
Io	3.52	1.79×10^2	$\sim 1 \times 10^{-10}$	~ 110 $SO_2(\sim 1)$	—

* Reading from left to right, these variables are the following: the object's mean density, in units of gm/cm^3 ; acceleration of gravity, in cm/s^2 ; surface pressure, in bars; surface temperature, in K —the numbers in parentheses are values of effective temperature; major gas species—the numbers in parentheses are volume mixing ratios; minor gas species—the numbers in parentheses are fractional abundance by number in units of ppm; aerosol species—the numbers in parentheses are typical values of the aerosols' optical depth in the visible. The numbers in this table were derived from the following sources: Blanco & McCuskey (1961), Hunten (1977), Jaffe et al (1979), Kumar (1976), Pearl et al (1979), Pollack & Black (1979), Pollack et al (1979b), Rages & Pollack (1979), Ridgway et al (1976), Rossow (1978), and Weidenschilling & Lewis (1973).

^b These mixing ratios refer to typical values at the surface.

^c These mixing ratios pertain to the region above the cloudtops.

^d The sulfuric acid aerosol resides in the lower stratosphere, while the sulfate, etc. aerosols are found in the troposphere, especially in the bottom boundary layer.

^e The ice clouds are found preferentially above the winter polar regions. Dust particles are present over the entire globe.

^f These mixing ratios pertain to the stratosphere.

classes of ancient channels appear to have been formed by running water and may require a much more massive atmosphere for their genesis, one capable of creating a strong greenhouse warming (Pollack 1979). What factors control these and other changes in the properties of planetary and satellite atmospheres?

In this paper, we review our current understanding of the origin and evolution of the atmospheres of solar system objects and assess our ability to answer the above questions. In the first part of the paper, we describe physical processes that control this evolution in an attempt to develop a set of general principles that can help to guide studies of specific objects. In the second part, we discuss the planetary and satellite atmospheres of the inner solar system objects and critically consider in each case current hypotheses on their origin and evolution, including a few new ones of our own. We regret that space permits only a cursory discussion of the atmospheres of objects in the outer solar system. The giant planets have been adequately treated elsewhere (Cameron & Pollack 1976, Pollack et al 1977, 1979a).

Several review articles touch on some of the topics discussed here. Among these are papers by Shemansky & Broadfoot (1977) on the exospheric atmospheres of Mercury and the Moon; Hunten & Donahue (1976) on the escape of light gases from the atmospheres of the terrestrial planets and Titan; Pollack (1979) on climatic changes on the Earth, Mars, and Venus; Cameron & Pollack (1976) on the formation and evolution of the giant planets; Hunten (1977) on Titan's atmosphere; and McElroy (1976) on photochemical processes in planetary atmospheres; and books by Walker (1977) and Holland (1978a) that treat the geochemical cycles that control the Earth's atmospheric composition (Walker's book also contains some discussion of the atmospheres of the other terrestrial planets).

PHYSICAL PROCESSES

In this section, we discuss the physical processes that determine the chemical composition and mass of a planetary or satellite atmosphere at a given epoch and the ones that cause long term changes in these properties.

Sources of Atmospheric Gases

There are four major sources of the gases in planetary and satellite atmospheres: the primordial solar nebula, the solar wind, colliding bodies, and the object's interior. Table 2 summarizes the time period during which each of these sources is expected to be most effective and the dominant volatile-forming elements they contain, in approximate ranked order.

Table 2 Nature of the sources of planetary and satellite atmospheres

Source	Elemental composition ^a	Time period of greatest potency ^b
Primordial solar nebula	H > He > O > C > N > Ne > Mg > Si > Fe > S > Ar	4.6
Solar wind	H > He > O > C > N > Ne > Mg > Si > Fe > S > Ar	~4.6 ^c
Colliding bodies	H ₂ O > S > C > N	~4.6–4.0
Interior	H ₂ O > C > Cl > N > S	~4.6–4.0 ^d

^a The compositions given here are based on solar abundances, carbonaceous chondritic meteorites, and terrestrial "excess volatiles" for the primordial solar nebula and solar wind, colliding bodies, and the interior, respectively (Cameron 1970, and Walker 1977). Only the elements that help to constitute key volatiles are considered here.

^b Time in aeons from the present, with 4.6 taken as the time of solar system formation.

^c However, it is the present day solar wind that is relevant for the atmospheres of Mercury and the Moon.

^d Later, episodic outgassing can also be important. This is particularly true in the case of Io, where the composition of the outgassed material may have changed with time.

Justification for the entries in Table 2 will be given below. All four sources are most potent during the early history of the solar system.

1. PRIMORDIAL SOLAR NEBULA The term "primordial solar nebula" refers to the diffuse cloud of gas and dust that formed the source material from which all solar system objects, including the Sun, were formed. Presumably, the elemental composition of the solar nebula was very similar to that characterizing the outer portions of the current Sun. Radioactive dating of meteorites, lunar samples, and terrestrial rocks indicates that planet formation took place about 4.6 billion years ago, with the epoch probably spanning less than several hundred million years (e.g. Wasserburg et al 1977). Although the solar nebula is the ultimate source of all planetary and satellite constituents, including volatiles, we consider here only the direct way in which it may have contributed to the formation of planetary atmospheres.

First consider satellites and terrestrial planets. After they had completely formed, their gravitational fields may have caused a nearby concentration of solar nebula gases. A portion of the material may then have been retained after the solar nebula dissipated. Whether this scenario was in fact followed depends on the relative timing of the completion of satellite and planetary formation and the disappearance of the solar nebula and on the effectiveness of the nebular dissipation process in stripping away such an early atmosphere. This type of atmosphere, as well as one due to an early intense solar wind, is frequently referred to as a "primary" atmosphere.

The solar nebula is the only plausible source for the massive atmospheres of the giant planets. The origin of these planets and their atmospheres will be discussed in the next section of this paper.

2. SOLAR WIND The solar wind is a magnetized and fully ionized gas that originates in the uppermost portions of the Sun's atmosphere and flows outward into interplanetary space. At the orbit of the Earth, typical values for the solar wind's temperature, velocity, number density, and flux are 2×10^5 K, 500 km/s, 5 particles/cm³, and 2×10^8 particles cm⁻² s⁻¹, respectively, for quiescent conditions (Walker 1977). At other distances from the Sun, the flux scales crudely as the inverse of the distance squared. The composition of the solar wind is approximately, but not exactly, the same as the Sun's. In the case of an object that lacks both an appreciable atmosphere and intrinsic magnetic field, such as the Moon, the solar wind flows down to the object's daytime surface, before being deflected around the object. In the case of objects with an appreciable magnetic field, such as the Earth and Mercury, or objects with an appreciable atmosphere and hence ionosphere, such as Venus, the solar wind is deflected well above the object's surface, although some material may leak in through the interface between the solar wind and the object's magnetic field or ionosphere.

Consider first objects such as Mercury and the Moon that lack appreciable atmospheres. In such cases, temporary capture of solar wind material occurs as the result of charged particles striking surface material, being temporarily held by the surface material, becoming neutralized, and ultimately being released back into the atmosphere. Once neutralized, the solar wind derived gases can no longer be removed immediately by being caught on magnetic field lines within the solar wind and swept away. According to the classical model of this capture process, the surface grains quickly become saturated with solar wind derived neutrals so that, as new material is added to the surface, an equal amount of older gases leave and enter the atmosphere with a Maxwell-Boltzmann distribution of kinetic energies and a temperature equal to that of the surface (Hodges 1975). Important modifications to the above first order description are given in Hodges (1975) and Shemansky & Broadfoot (1977).

In principle, the solar wind could also be an important source of gases present in more massive atmospheres, such as those of Venus, the Earth, and Mars. For example, if all the solar wind incident upon Venus was added to its atmosphere, a very unlikely situation, the number of H atoms added cumulatively over the age of the solar system would equal 6×10^{25} atoms/cm², equivalent to an H/C ratio of 4×10^{-2} . In this case, the solar wind could constitute an important source of H₂ in Venus'.

atmosphere. Similarly, the solar wind could be an important source of He and Ne. However, proceeding in an analogous manner as for H, we find that the current solar wind fails by orders of magnitude to supply the amount of C, N, and Ar known to be present in Venus' atmosphere. Analogous comparisons hold for the Earth and Mars.

The very early solar wind may have been much more intense. A popular theme in the literature has been the dissipation of the solar nebula with a "T-Tauri" type solar wind, by analogy with the high outflow rates that characterize some of the earliest stages of stellar evolution (see, for example, Cameron & Pollack 1976). Such a wind could also add much material to the atmospheres of solar system objects during the earliest history of the solar system.

3. COLLISIONS WITH ASTEROIDS AND COMETS The highly cratered surfaces of the Moon, Mars, and Mercury attest to the large cumulative mass brought into them and into other solar system bodies through impacts with much smaller stray objects, such as asteroids and comets, whose initial orbits were perturbed into planet- and satellite-crossing orbits. Some asteroids in the asteroid belt and some with Earth-crossing orbits resemble, in their spectral characteristics, carbonaceous chondrites, a volatile-rich type of meteorite (Morrison 1977). When they enter the inner solar system, comets are extremely volatile-rich. However, because the orbital period of a short period comet (\sim several years) is much smaller than its residence time in the inner solar system prior to impact ($\sim 10^8$ years; Wetherill 1975), a "dead" comet nucleus loses much of its volatiles prior to impact. Nevertheless, it still may be as volatile-rich at this point as a carbonaceous chondrite. Thus, a significant amount of volatiles may have been added to inner solar system bodies through impacts with small stray objects. Small stray objects may be even more volatile-rich when they strike bodies in the outer solar system, since little evaporation takes place at these large distances prior to impact. At the typical velocities of impact (~ 10 km/s), all the volatiles are released into the impacted body's atmosphere.

Comparison of crater densities on various areas of the Moon with the age of the terranes, as established from returned lunar samples, indicates that there was a much higher flux of impacting objects during the Moon's first 700 million years than at subsequent times (Wetherill 1975). Since gravitational perturbations by Venus and the Earth change the orbits of stray bodies into ones that, in most cases, cross the orbits of all the terrestrial planets (Wetherill 1975), a similar bombardment history must have been experienced by all bodies in the inner solar system.

We can make a crude estimate of the importance of small body colli-

sions as a source of planetary atmospheres subsequent to planet formation by comparing the mass of water brought in by these bodies over the lifetime of the Earth with the amount of water contained in the Earth's oceans. The observable crater population on the moon's surface was produced by impacting bodies having a cumulative mass of about 10^{21} gm, with most of the mass contained in the largest impacting objects, such as the one that produced the Imbrium basin (Wetherill 1975). For the moment, let us neglect the highly uncertain, additional mass of objects which formed craters that were subsequently obliterated. Note that obliterated basins are of greatest interest in this regard. Therefore, allowing for differences in surface area and impact probability per unit area (Wetherill 1975), we estimate that a cumulative mass of about 2×10^{22} gm impacted the Earth over its lifetime. If we assume that the impacting objects, on the average, had a water content of 10%, a value typical of the more volatile-rich carbonaceous chondrites (Mason 1962), then these impacts added about 2×10^{21} gm of water. The above water content could well be a gross overestimate. Nevertheless, even with this generous assumption, the above estimate of water brought in by impacts is about three orders of magnitude smaller than the mass of water contained in the Earth's oceans (Turekian & Clark 1975). Similar differences occur when the carbon brought in by impacts is compared with the amount of carbon-containing material that resided at some time in the Earth's atmosphere (Turekian & Clark 1975). Therefore, impacting bodies may not represent an important source of the major volatiles for at least the Earth's atmosphere subsequent to the Earth's formation. But, in view of the crudeness of the above calculation, such as our neglect of obliterated lunar basins, it is premature to make a definitive judgment at this point. Also, impacting objects might be an important source of certain volatiles in cases where the planetary interior is greatly depleted in these volatiles, such as perhaps S and H₂O in the case of Venus (Lewis 1974).

4. INTERIOR SOURCES The grains that accreted to form planets and satellites may have contained volatile-forming compounds. After the planet or satellite formed, heating of its interior in conjunction with associated volcanism and tectonic activity resulted in the release of some of the stored volatiles into the atmosphere. Some release also occurred during planetary accretion. Below, we discuss the composition of the volatile-forming compounds, the sources and timing of interior heating, and the composition of the outgassed volatiles.

Meteorites provide useful clues on the chemical composition of the material that was initially present inside terrestrial planets and satellites,

since certain classes of meteorites have undergone relatively little thermal or chemical evolution since their formation. However, it is probably a mistake to model quantitatively inner solar system bodies after certain classes of meteorites since meteorites originated in only limited regions of the solar system. Table 3 summarizes the principal chemical compounds found in meteorites that contain volatile-forming elements. Also given in the table are the atmospheric gases that contain the volatile element and the temperature within the solar nebula at which it is thermodynamically possible to form the chemical compound. Except for the rare gases, the volatile elements form an integral part of the crystal structure of their associated chemical compounds. Thus, heating to high temperatures is required for the release of these volatile elements, an act which destroys the host mineral. Also note that, except for the rare gases and water of crystallization, none of the volatile elements appear with the same chemical makeup as their corresponding atmospheric gases. Such conversions can take place in the air spaces of magma chambers. For example, C originating in organic compounds can obtain O needed to form CO₂

Table 3 Chemical compounds in meteorites that contain volatile-forming elements^a

Volatile gas	Volatile elements	Chemical compound	Formation temperature
Water	H	Organics	≤ 750 K
		Hydrated minerals (water of crystallization and hydroxyl groups)	~ 150–450 K
Carbon dioxide	C	Organics	≤ 750 K
Methane		Graphite	
Carbon monoxide		Carbonate ^b	
Nitrogen	N	Organics	≤ 750 K
Ammonia		Ammonium salts ^b	
		Nitrides	
Sulfur dioxide	S	Troilite (FeS) ^c	500–700 K
Hydrogen sulfide		Sulfates ^b	
		Free sulfur	
		Organics	≤ 750 K
Hydrogen chloride	Cl	Apatite (Ca ₅ (PO ₄) ₃ Cl)	
		Lawrencite (FeCl ₂)	
		Organics	≤ 750 K
Rare gases	rare gases	Occluded gases Radioactive elements ^d	

^a Based on data given in Mason (1962) and Lewis (1974).

^b Probably an alteration product.

^c Dominant sulfur compound.

^d ⁴⁰K is a source of ⁴⁰Ar and U and Th are sources of helium.

from either the oxygen released by dissociated water vapor or the oxygen contained in ferro magnesian silicates and magnetite. It is interesting to observe that organic compounds contain all the volatile elements given in Table 3. Finally, in addition to the rare gases found occluded within minerals, the decay of radioactive elements also serves as a source of certain rare gases (see footnote d on Table 3).

The above discussion has relevance for objects in the inner solar system and possibly for Io. In the case of satellites of the outer solar system, such as Titan, temperatures below about 200 K within the circum-planetary nebula of their birth may have permitted ices to condense and therefore to be incorporated within the satellite-forming materials (Lewis 1974, Cameron & Pollack 1976). As the temperature is lowered, first water ice becomes thermodynamically stable, followed by ammonia hydrate and then methane clathrate ($\text{NH}_3 \cdot \text{H}_2\text{O}$, $\text{CH}_4 \cdot 6\text{H}_2\text{O}$). These interior ices can serve in a rather direct fashion as sources of atmospheric water vapor, ammonia, and methane.

There are three major epochs of strong heating during which volatiles were released into planetary and satellite atmospheres: accretion, global internal differentiation, and local volcanism. Especially during the later stages of planetary and satellite formation, accreted material may be heated to high temperatures due to ablation in the object's very early atmosphere or high velocity impact with its surface (Jakosky & Ahrens 1979). However, if the best current values for the time scale of planetary accretion are used ($\sim 10^8$ years), then the surface temperature of the outer three terrestrial planets remained low enough to permit the re-incorporation of the released H_2O and CO_2 into these bodies due to chemical reactions with surface minerals, followed by burial during later accretion (Jakosky & Ahrens 1979). Rare gases and nitrogen may have remained in the atmosphere. Below, we will give some evidence that the subsurface temperatures may have been quite high during accretion. If so, complete reincorporation may not have occurred.

During the later stages of accretion and/or thereafter, terrestrial planets and large satellites underwent global internal differentiation, resulting in the appearance of a low density crust and a high density core. Opinions on the degree of initial chemical zonation have ranged the full gamut from a totally homogeneous mixture of low and high temperature condensates to a fully inhomogeneous model with iron and other core-forming materials already located near the object's center (see, for example, Jakosky & Ahrens 1979, Walker 1977). In our opinion, while materials of different volatility classes may have formed at different times from the primordial solar nebula, accretion into a completely segregated body seems unlikely. Hence, some core formation probably

took place during the internal differentiation event that generated the crust and, most importantly, some metallic iron was initially present in the upper mantle.

Age dating of returned lunar samples indicates that the Moon's sialic crust was formed during the first several hundred million years (Wasserburg et al 1977). In order to create a 60-km thick crust, as implied by seismic measurements, a "magma" ocean with a minimum depth of several hundred kilometers had to be present close to the surface during this epoch of internal differentiation. Portions of the surface of Mars and Mercury exhibit a high density of craters, comparable to that of the lunar highlands (Toksöz et al 1978, Wetherill 1975). Since the lunar highlands record the early epoch of intense meteorite bombardment and since the bombardment flux is not expected to vary greatly throughout the inner solar system (Wetherill 1975), crustal formation and associated outgassing took place during the first billion years of the history of Mars, Mercury, and, by implication, Venus and the Earth.

Age dated lunar samples also provide a good definition of the timing of subsequent igneous activity on the Moon (Wasserburg et al 1977). Mantle-derived magmas reached the lunar surface, locally and episodically, from about 4.4 to 3.1 billion years ago, but no sizeable expression of igneous activity on the surface occurred at later times, due probably to lithospheric thickening. Currently, this rigid outer region of the Moon extends to a depth of 700–1000 km. Extensive lithospheric thickening is expected to be delayed to progressively later times for progressively larger objects than the Moon (Toksöz et al 1978). Hence, basaltic volcanism and associated outgassing span larger time intervals for larger objects.

Figure 1 illustrates the results of thermal history models of an initially homogeneous Moon, Mars, Mercury, and Venus that are consistent with the above and other relevant constraints (Toksöz et al 1978). In order to have global internal differentiation occur at early times, the temperature of the outer layers of these bodies was assumed to be at or close to the melting point. Consequently, it is quite conceivable that much of the volatiles released during the later stages of accretion were never effectively reincorporated back into the body's interior. Furthermore, given the extensive melting associated with accretion and internal differentiation, much of the juvenile volatiles may have been released during the first billion years of the solar system for inner solar system objects. Finally, the degree of early outgassing may have been size-dependent, with the smaller bodies outgassing less effectively due to a smaller amount of heating per unit mass by accretional processes and core formation (Toksöz et al 1978, Jakosky & Ahrens 1979).

The next major period of outgassing is associated with later partial

melting of portions of the mantle. For small objects such as the Moon, this epoch ended several billion years ago as the lithosphere became too thick. For objects of the size of the Earth, this epoch is still occurring and may have spanned much of the object's history. Although most of the juvenile volatiles may have been released during the first two epochs, this last epoch is important not only for supplying new material, but also in recycling volatiles that were outgassed, but subsequently incorporated into surface rocks.

An understanding of the thermal history of the satellites of the outer solar system is at a much more primitive stage than the study of inner solar system objects. However, it appears that Io and Titan, among others, are probably large enough to have undergone extensive differen-

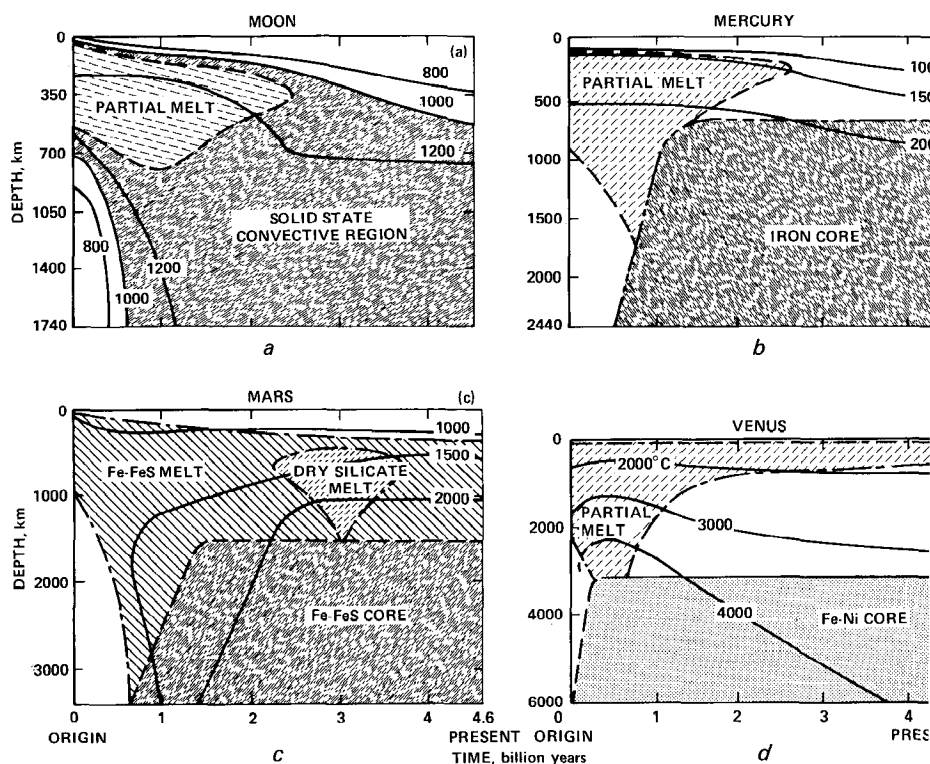


Figure 1 Thermal evolution of the interiors of the Moon (a), Mercury (b), Mars (c), and Venus (d) as a function of time from the completion of planetary formation (0 years). The curves in these figures are isotherms, with their associated numbers being temperatures in °C. In all cases, the model planets were assumed to have a homogeneous composition at the initial epoch. From Toksöz et al (1978).

tiation (Consolmagno & Lewis 1977). In the case of Io, intense tidal heating throughout most of its history appears to have resulted in a very thin lithosphere and extensive active volcanism (Peale et al 1979, Smith et al 1979).

Finally, we discuss the chemical composition of the outgassed volatiles. Considerations of thermodynamic equilibrium provide a useful first approximation to the state of oxidation of gases vented from the interior (Holland 1962). It is useful to distinguish between two stages at which thermodynamic equilibrium may apply. During stage 1, the gases come to thermodynamic equilibrium with their source magma at partial melting temperatures (1500 K for mantle silicates). Volatiles outgassed into the atmosphere have a composition similar to this equilibrium situation. Once outgassed, the volatiles cool to temperatures similar to that of the surface and some gases are severely depleted due to condensation. During stage 2 gases may achieve a new state of thermodynamic equilibrium appropriate to the revised set of conditions.

In order to illustrate these concepts more clearly, we consider a terrestrial planet having a rock and volatile content similar to that of the Earth (Holland 1962). Thus, ferro magnesian silicates are abundant and water is the chief volatile. According to Holland (1962), the state of oxidation of iron in the volatile source region controls the oxidation state of the gases during stage 1. At temperatures characteristic of silicate magma, water vapor partially dissociates into hydrogen and oxygen. But the oxygen partial pressure is severely limited by the iron-containing rocks and hence a net reduced state with some free hydrogen but little oxygen results for the volatiles. Suppose first that some metallic iron is present, as might be the case prior to the completion of core formation. In this case, the hydrogen partial pressure approximately equals that of water vapor. Under these conditions CO is the dominant C-containing gas, H₂S the dominant S gas, and N₂ the dominant N gas. During stage 2, there is more molecular hydrogen, at least initially, than carbon-containing gases. As a result of this fact and the much lower temperatures, methane may become the dominant carbon gas. Also, some N₂ may be converted to ammonia. H₂S remains the dominant S gas. Figure 2 illustrates the dependence of the oxidation state of C and N gases on the hydrogen partial pressure for room temperature conditions, when only thermodynamic equilibrium is considered.

Next we consider a situation more appropriate to the current oxidation state of the Earth's mantle. No metallic iron is present, the rocks contain mostly FeO, but they also contain some Fe₂O₃. Under these conditions, stage 1 is characterized by a hydrogen partial pressure of about 10^{-2} that of water vapor, and CO₂, SO₂, and N₂ are the dominant C, S, and N

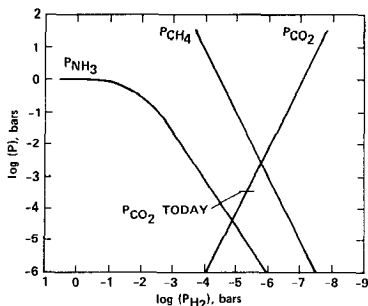


Figure 2 Relationship between the partial pressure of H_2 , P_{H_2} , and the partial pressures of CH_4 , CO_2 , and NH_3 , P , under conditions of thermodynamic equilibrium at room temperature. From Holland (1962).

gas species, respectively. During stage 2, some but not all CO_2 and CO may be converted to CH_4 , the conversion being limited by the abundance of H_2 . Also CO is rapidly converted to graphite and CO_2 . If, as is likely, there is more H_2 than SO_2 , all the SO_2 may be converted to H_2S . Alternatively, SO_2 is largely eliminated by surface weathering reactions. Essentially all the N volatiles are in the form of N_2 .

It is quite conceivable that kinetic limitations may prevent thermodynamic equilibrium from being achieved during stage 2. In this case, even if much of the outgassing from the interior took place while metallic iron was present in the upper mantle, only trace amounts of CH_4 and NH_3 would be present initially in the atmosphere. Thus, both the uncertainty in possible kinetic inhibitions during stage 2 and in the fraction of time metallic iron was present in the upper mantle lead to very large possible ranges for the oxidation state of C and N in early atmospheres.

A further complication is created by the distinct possibility that much of the initial release of volatiles may have occurred during the accretion phase. In this case, both possibly elevated temperatures, reflecting those in the surrounding solar nebula, and sizeable partial pressures of hydrogen, originating from the nebula, may have created a more favorable circumstance for the creation of an early, highly reducing atmosphere.

Sinks of Atmospheric Gases

Light gases can escape to space, while many chemically reactive gases as well as the more easily condensable ones can be severely depleted from the atmosphere by being incorporated into near-surface reservoirs under conditions of moderate or low surface temperature. In the case of the satellites and the terrestrial planets, only the rare gases of intermediate molecular weight, such as neon, argon, and krypton, appear to be largely immune to such loss processes.

1. **ESCAPE TO SPACE** Gases can escape from the top of planetary atmospheres through a variety of processes that include hydrodynamical flow, thermal evaporative loss (Jeans escape), photochemical escape, and loss by charge or energy exchange. Each of these processes is discussed below. The reader is referred to the review article by Hunten & Donahue (1976) for a more detailed presentation of this material.

Hydrodynamical loss involves mass outflow of atmospheric gases into interplanetary space at supersonic speeds. Thus, there is no mass fractionation of the gases present in the upper atmosphere, but there may still be a fractionation between the gas species present in the lower and upper atmospheres due to diffusive separation below the altitudes of supersonic flow. Hydrodynamical loss occurs when $H_c > 1/2 r_c$, where H_c and r_c are the scale height of the lightest gas and the distance from the body's center to the critical level (Hunten 1973). Critical level or base of the exosphere refers to the place at which the mean free path for collisions equals the scale height. For almost all atmospheres, $H_c < 1/2 r_c$ and hence hydrodynamical escape does not occur. Important exceptions to this conclusion include the solar wind; ion flow in the polar regions of the Earth; and the blowoff of a hypothetical hydrogen-rich atmosphere of Titan (Hunten 1973).

In the absence of hydrodynamical loss, light gases can escape to space through thermal evaporation at and above the critical level. To first order, all atoms having an upward-directed velocity greater than the gravitational escape velocity and lying within one mean free path of the top of the atmosphere are lost to space. The fraction of atoms having velocities in excess of the escape velocity can be calculated approximately from the Boltzmann velocity distribution at the exospheric temperature, although some depletion in the high velocity tail of the distribution results from escape (Chamberlain 1963). The classical Jeans equation for the escape flux, F_j^i , for constituent i may be written as (Hunten 1973):

$$F_j^i = n_c^i W_c^i = n_c^i \frac{U}{2\sqrt{\pi}} (1 + \lambda_c^i) \exp(-\lambda_c^i) \quad (1)$$

where

$$U = (2kT/m^i)^{1/2}, \quad \lambda_c^i = r_c/H_c^i, \quad H_c^i = kT_c/m^i g_c$$

and n , W , k , T , m , H , and g denote number density, "effusion" velocity, Boltzmann's constant, temperature, molecular weight, scale height, and acceleration of gravity, respectively. Because $\lambda_c^i \sim m^i$ and $F_j^i \sim \exp(-\lambda_c^i)$, only the lightest gases escape at appreciable rates through thermal evaporation.

There are three possible controls on the value of the thermal escape rate, F_j^i : the exospheric temperature, T_e ; the rate at which the escaping atom diffuses to the exosphere from the atmosphere beneath; and the rate at which the escaping gases are supplied chemically. T_e is the controlling factor when it is sufficiently low.

Now, suppose that T_e is sufficiently large that diffusion from the lower atmosphere limits the escape rate (Hunten 1973). In this case, the diffusion rate and hence the escape rate are approximately equal to the limiting flux F_h^i , evaluated at the homopause:

$$F_j^i \cong b_h^i f_h^i / H_h^a \quad (\text{if } m^i \ll m^a \text{ and } f_h^i \ll 1) \quad (2)$$

where b_h^i and f_h^i are the binary collision coefficient and the number mixing ratio of species i to the rest of the atmosphere, respectively. Scripts h and a refer to the homopause level and the rest of the atmosphere, respectively. Homopause refers to the level at which the eddy mixing coefficient, K , equals the diffusion coefficient of species i , D^i . More general expressions are given in Hunten (1973). The corresponding diffusion velocity, W_i , is given by $D^i/H_h^a = K/H_h^a = W_i$. Diffusion rather than exospheric temperature is the rate-limiting process when $W_i < W_e$. In such a situation, the number density at the exospheric level, n_e^i , is adjusted so as to insure that $F_j^i = F_h^i$. In the more general situation of several escape processes contributing to the loss at the top of the atmosphere, but diffusion being the rate-limiting step, Equation (2) remains

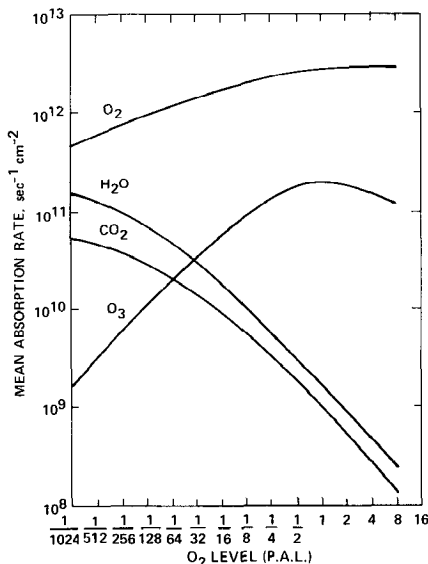


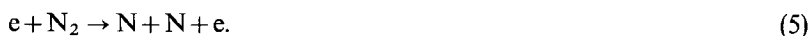
Figure 3 Mean absorption rates of UV photons capable of dissociating water vapor for various atmospheric species as a function of the oxygen level relative to today's level (= 1 P.A.L.). From Brinkman (1969).

valid and F_i^1 is equal to the sum of the loss fluxes at the top of the atmosphere.

In evaluating Equation (2) at the homopause, f_h^i may be set equal to the mixing ratio of all *i*-containing species. For example, if atomic hydrogen, but not molecular hydrogen, escapes efficiently from the exosphere and molecular hydrogen is the chief H-containing species at the homopause, f_h^i is simply twice the molecular hydrogen mixing ratio at the homopause. In the absence of condensation, the mixing ratio of all *i*-containing species remains constant below the homopause, despite photochemical transformations. Hence f_h^i can be evaluated by using data on abundances in the stratosphere.

As indicated by Equation (2), $F_i^1 \sim f_h^i$. As f_h^i increases, eventually a point is reached at which the loss rate becomes limited by the rate at which gas species containing species *i* can be converted by photochemistry into species *i*. In this case, the escape rate of species *i* may be limited by the flux of solar photons needed for the rate-determining photochemical step. For example, Figure 3 illustrates the photon-limited rate at which water vapor is photodissociated into hydrogen and oxygen as a function of oxygen content for an atmosphere containing 5 ppm H₂O and 330 ppm CO₂ above the tropopause and for the current solar UV flux at the Earth (Brinkman 1969). The ozone content has been assumed to be proportional to the oxygen abundance. For other choices of water vapor or carbon dioxide mixing ratio, the appropriate curve will scale approximately linearly with mixing ratio, under the constraint that the sum of all curves for a fixed oxygen level is an invariant.

When the velocity distribution is dictated by thermodynamic equilibrium as is appropriate for Jeans escape, only the lightest atoms escape at appreciable rates. However, it is possible to generate medium weight atoms with speeds in excess of the escape velocity by highly exothermic photochemical reactions. When these reactions occur above the base of the exosphere, about half of the fast atoms (the ones with upward-directed velocities) are lost to space. There are three types of photochemical reactions that can lead to photochemical escape: dissociative recombination, photodissociation, and dissociation by photoelectrons. Examples of each of these types, which are relevant for the escape of C, O, and N atoms from Mars, are (McElroy 1972, McElroy et al 1976)



Photochemical escape provides an important loss mechanism for C, N,

and O in the case of Mars (McElroy 1972) and for H in the case of Venus (Kumar et al 1978).

Another important loss process involves charge exchange between a very energetic or "hot" proton and a neutral atom (Hunten & Donahue 1976). In the case of unmagnetized planets, such as Venus and Mars, the solar wind is the source of the hot proton. The slow atom, which acquires a charge through the charge-exchange reaction, is trapped around magnetic field lines in the solar wind and is swept away from the planet. The very "hot" proton, which is neutralized by the reaction and therefore is no longer tied to the solar wind's magnetic field lines, escapes to space either directly, if its motion is away from the planet, or indirectly, following collisions with atmospheric atoms. Thus, there is a net loss of the neutral atom as a result of the charge-exchange reaction. Photoionization can also convert a neutral atom to an ion that can be picked up by the solar wind (Kumar 1976).

The capacity of the solar wind to pick up atmospheric atoms is limited (Cloutier et al 1969). If it adds a mass more than $\sim 9/16$ of its initial mass, a shock layer forms and the solar wind flow is diverted further from the planet so that this limiting mass factor is not exceeded. Assuming solar wind sweeping operates at maximum efficiency, one may write this escape flux, $F_{s.w.}$, as (Hunten & Donahue 1976)

$$F_{s.w.} \cong 0.17 \phi H/r, \quad (6)$$

where ϕ , H , and r are the flux of solar wind protons, atmospheric scale height at the level of the solar wind, and distance from the center of the planet to the interface with the solar wind near the limb, respectively. Solar wind sweeping represents an important loss process for C and N from Mars (McElroy 1972), for H from Venus (Kumar et al 1978), and for all the constituents of the lunar atmosphere (Kumar 1976).

In the case of planets with magnetic fields, such as the Earth, the solar wind is deflected far above any significant atmosphere, but charge-exchange reactions within the magnetic cavity can still be important. In particular, charge-exchange reactions between atoms in the uppermost region of the exosphere and very hot protons trapped by the planetary magnetic field, a component of the plasmasphere, result in a fast atom, which escapes, and a trapped thermal ion. The escape flux in this case is given by Equation (7) of Hunten & Donahue (1976). This process provides an important loss mechanism for H from the Earth at present (Hunten & Donahue 1976). Since the solar wind provides the energy to heat the plasmasphere, there is again a limit associated with the loss rate, although a higher one than in the unmagnetized planet case because of a higher cross section for interaction. A similar mechanism for escape of

oxygen from the Earth's atmosphere has recently been proposed by Torr et al (1974). Energetic O^+ ions produced in magnetic storms could charge-transfer with a thermal oxygen atom and result in producing a "hot" O atom capable of escaping from the Earth's gravitational field.

The environment of the satellites of the outer planets may be dominated by the magnetosphere of their parent planets rather than the solar wind. In this case, potentially important loss processes include charge-exchange reactions with the magnetospheric plasma and energy exchange with high energy magnetospheric particles. In the latter case, a given magnetospheric particle may be capable of ejecting a number of atmospheric particles by elastically scattering them to energies far in excess of the escape energy, with the scattered particles eventually escaping after suffering a number of collisions and energy losses with other atmospheric particles. We note that it may suffice for the escaping particles to simply reach the magnetosphere proper, where they can become ionized and swept away by the magnetic field.

2. LOSS TO SURFACE AND INTERIOR RESERVOIRS In the case of satellites and terrestrial planets, a large proportion of many gas species that were present at some time in the atmosphere currently reside in near-surface reservoirs as a result of condensation, adsorption, and chemical weathering. In the case of the outer planets, certain gas species may be partially removed from the observable atmosphere to the deep interior because of the onset of fluid immiscibility.

When the partial pressure of a gas reaches its saturation vapor pressure close to the surface, the gas begins to condense, with the condensate ultimately being removed to the surface. The key variable in such cases is the surface temperature since the saturation vapor pressure depends exponentially on it. Such a dependence implies that only modest changes in surface temperature can result in quite substantial changes in the amount of condensible gases in the atmosphere. Water is a good example of a condensible gas. In the case of the Earth, there is about five orders of magnitude more water in the oceans than in the atmosphere. Other examples include H_2O and CO_2 in the case of Mars, CH_4 in the case of Titan, and SO_2 in the case of Io.

When fine-grained sedimentary deposits are present on the surface, some gases, particularly ones with large polarizabilities, become physically adsorbed onto the surface of the grains. For a given sediment, the amount of gas of a given type that is adsorbed onto a unit volume of the sediment is a function of both the sediment's temperature and the gas's partial pressure. Figure 4 illustrates this dependence between CO_2 gas and both a fine-grained clay (nontronite) and a coarse basalt powder,

for conditions appropriate for Mars. For a fixed temperature and partial pressure, the total amount of gas adsorbed onto surface deposits is proportional to the "effective" area of the grains and the total volume of the sedimentary layer in contact with the atmosphere. Thus, finer-grained deposits are more effective reservoirs than coarser-grained ones (cf Figure 4). The fine-grained regolith of Mars may contain much more adsorbed CO₂ than is present in the atmosphere (Fanale & Cannon 1979). In the case of the Earth, more xenon may reside in shales than in the atmosphere as a result of adsorption (Fanale & Cannon 1971).

Sedimentary, metamorphic, and igneous rocks that are brought to a body's surface by tectonic processes are generally not in thermodynamic equilibrium with their new environment, one characterized by much lower temperatures than those of the body's interior, a variety of atmospheric gases, and, in the case of the Earth, liquid water. Consequently, some of the mineral constituents of surface rocks undergo chemical reactions with atmospheric gases, which convert the former to more stable phases. This "chemical weathering" represents an important sink for many atmospheric gases. For example, calcium-bearing silicates react with CO₂ to produce calcium carbonate, which may be represented schematically as (Urey 1952)

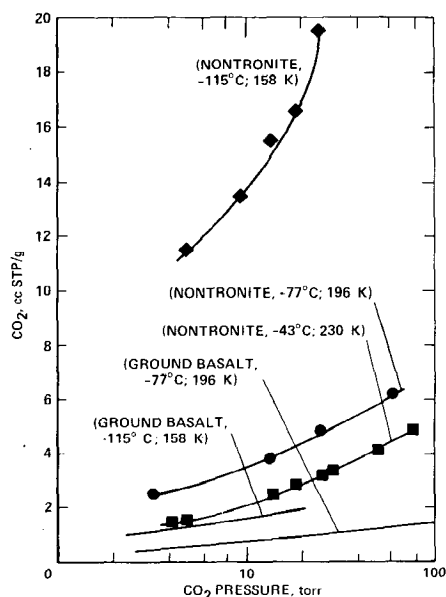


Figure 4 Amount of adsorbed CO₂ (vertical ordinate) as a function of the partial pressure of CO₂ gas for two types of powdered materials and several temperatures. From Fanale & Canon (1979).

Ideally, the CO_2 pressure in the atmosphere is adjusted until thermodynamic equilibrium is achieved. However, as explained in a later subsection on the Earth, the true situation can be much more complicated on a planet that has liquid water and active tectonism.

The rate at which atmospheric gases are lost as a result of chemical weathering is a function of the erosion rate, the fraction of rock material that undergoes chemical weathering, and the degree of completion of the weathering reactions. Quite possibly, the Earth has a uniquely high erosion rate among solar system bodies due to the occurrence of rainfall and various biological processes. Chemical weathering is an important loss process for CO_2 and O_2 in the case of the Earth. Its importance for other objects with atmospheres is less clear.

Conversion Processes

PHOTOCHEMISTRY Photochemical reactions within the atmosphere result in the creation of many trace constituents; the conversion of some gases to aerosols, which are subsequently removed rapidly from the atmosphere; the conversion of some gases irreversibly to other gases; and the production of light constituents, especially atomic hydrogen, which can escape from the top of the atmosphere.

Trace constituents are of particular interest if they affect the solar or thermal radiation. An obvious and very important example is ozone in the Earth's atmosphere, which prevents biologically harmful solar UV radiation from reaching the Earth's surface. Ozone is generated through the photodissociation of molecular oxygen. Recent calculations of its abundance have taken into account not only the chemistry of O, O_2 , and O_3 , but also that of hydrogen-, nitrogen-, and chlorine-containing compounds, which exert important catalytic control over the ozone destruction rate (Logan et al 1978).

The conversion of gases to particles is an effective mechanism for reducing the gas content of an atmosphere. The very low abundance of SO_2 in the Earth's atmosphere is partly the result of its rapid conversion into sulfate particles, the conversion being initiated by reactions with such radicals as OH. Also, as discussed later, the production of aerosols in Titan's atmosphere may constitute a long term sink for their precursor gases.

As an atmosphere evolves, gas species may become irreversibly converted into other gas species. For example, as an atmosphere becomes more highly oxidized, photochemical reactions can irreversibly convert ammonia into nitrogen, with this process being initiated by ammonia photodissociation (Kuhn & Atreya 1979). Such a change in oxidation state is driven by the loss of atomic hydrogen from the top of the

atmosphere, with photochemistry being responsible for converting other hydrogen-containing species into atomic hydrogen in the upper atmosphere (Hunten & Donahue 1976).

LIFE Within the solar system, the Earth has an apparently unique set of transformation processes, ones involving its biosphere. As discussed in the next section, photosynthesis by green plants is chiefly responsible for the large amount of free oxygen in the Earth's atmosphere. Living organisms are also important sources of such trace gases as nitrous oxide and methane.

Sources and Sinks of Aerosols

For our purposes, aerosols are an important part of an atmosphere both because they can strongly influence the radiation budget and because their formation may represent a sink of atmospheric gases, as discussed above. There are three important sources of atmospheric aerosols: winds, condensation, and photochemistry. When winds near the surface exceed a threshold speed, sand-sized particles are set into motion and dust-sized particles are put into suspension (Iversen et al 1976). Rising motions in the atmosphere cause a cooling of air parcels which may induce certain gas species to condense and form clouds. Photochemical conversion has been discussed above.

Aerosols generally remain in an atmosphere for only a short period of time (~day-year). Removal occurs by sedimentation, scavenging, evaporation, and precipitation (Rossow 1978). Gravity causes all particles to have a net downward velocity, with the fall velocity increasing monotonically with particle size and eddy mixing generally enhancing the net removal rate. Small particles may serve as nucleation centers for the formation of larger condensate particles, with the net result being an enhanced removal rate of the small particles because of a higher fall velocity. This process is responsible for the efficient removal of non-water aerosols from the Earth's troposphere and possibly the preferential deposition of dust particles in the Martian polar regions (Pollack et al 1979b). If a condensate particle falls to a region having unsaturated air, it evaporates, as occurs for small-sized water particles in the Earth's atmosphere. But rapid growth of particles within cloud regions through coalescence can produce large "precipitation"-sized particles, which fall quickly enough to survive to the surface.

Table 1 summarizes the principal aerosol constituents of planetary and satellite atmospheres. A much more detailed description of the above physical processes and their application to these atmospheres is given in Rossow (1978).

Drives for Climatic Change

The radiative properties and the general circulation of an atmosphere help to determine the climatic conditions at the surface and within the atmosphere. These aspects of an atmosphere are in turn related to the concentration of optically active gases, condensible gases, aerosols, and the total atmospheric pressure. Several external factors exert a strong control on these properties of an atmosphere. These factors include the solar input of energy at the top of the atmosphere, the interior heat flux, and tectonic and associated interior processes. Changes in climate and atmospheric properties result from changes in these factors (Pollack 1979).

In discussing the amount of solar energy incident at the top of an atmosphere, it is useful to distinguish between the total energy emitted by the Sun and the effect of astronomical factors, including an object's orbital and axial characteristics. Over the lifetime of the solar system, almost all models of the Sun's evolution predict that its luminosity has increased by several tens of percent, with the percentage increase ranging from about 25–40% (Sagan & Mullen 1972). [See, however, Canuto & Hsieh (1978) on the possible influence of cosmological factors on these results.] This leads to interesting questions concerning the generation of favorable climates on the Earth and Mars in their early history, despite the decreased solar luminosity then. These questions are discussed in the next section. On much shorter time scales of years to centuries, climatically significant, but much smaller changes in solar luminosity and/or spectral characteristics, especially in the UV, are known or suspected to have occurred (Eddy 1977).

On time scales of 10^4 – 10^6 years, the orbital eccentricity, axial tilt, and axial precession of the Earth and Mars undergo quasi-periodic variations (Ward et al 1974). Such changes result in seasonal and latitudinal alterations in the amount of incident sunlight. These variations may have played a role in causing ice ages on the Earth during the last several million years (Hays et al 1976) and in producing the layered terrain in the polar regions of Mars (Cutts 1973, Pollack 1979).

Internal heat fluxes are trivial compared to the solar input in the case of satellites and terrestrial planets. But even today the internal heat fluxes from Jupiter, Saturn, and Neptune are comparable to the solar inputs (Hubbard 1979). At earlier times, the internal heat fluxes may have been substantially higher (Pollack et al 1977).

A variety of internal processes affects the atmospheres and climates of satellites and planets. With the exception of the giant planets, the most important of these are ones related to the outgassing of juvenile and

recycled volatiles. In the case of the giant planets, internal phase changes can influence the atmospheric composition, as discussed earlier.

Finally, the atmosphere itself is not only affected by climate change, but, through loss processes to space, geochemical interactions with the surface, and regulation of surface temperature, it has a dynamic role. The complicated interrelationships between the atmosphere, surface, and interior make rigorous calculations of climate and atmospheric evolution impossible at the present time, although useful approximate methods have proved to be interesting and provocative. They form part of the subject matter of the next section of this paper.

ATMOSPHERES OF SOLAR SYSTEM OBJECTS

In this section, we review in sequential fashion current concepts on the origin and evolution of the atmospheres of the solar system objects listed in Table 1.

Origin of the Atmospheres of Venus, Earth, and Mars

Here, we consider relevant data that permit preliminary assessments of the major sources of the atmospheres of the outer three terrestrial planets and of the spatial distribution of the initial volatile endowment. The starting point for such an assessment is an estimate of the composition and amount of gases that, at some time, have been present in a planetary atmosphere—the volatile inventory. In the case of the Earth, reasonably good determinations of its volatile inventory can be obtained from the known composition of its atmosphere, in conjunction with estimates of the amount of volatiles stored in surface, crustal, and mantle reservoirs (e.g. the oceans and carbonate rocks; Turekian & Clark 1975). The high surface temperature of Venus implies that, to first approximation, all of its volatile inventory is presently in its atmosphere. Thus, atmospheric compositional measurements made in situ from the Pioneer Venus and Venera spacecraft provide good estimates of Venus' volatile inventory, except perhaps for water, as discussed in the subsection on Venus. Because of the low surface temperatures on Mars and a lack of information on the amount of volatiles present in surface and subsurface reservoirs, our knowledge of its volatile inventory is incomplete, despite the compositional measurements made in situ from the Viking spacecraft. Nevertheless, the abundance of rare gases, except possibly Xe, in the Martian atmosphere probably closely matches that of its volatile inventory (Anders & Owen 1977). Also, the observed $^{15}\text{N}/^{14}\text{N}$ isotopic ratio, which exceeds the terrestrial value by about 62‰, provides useful constraints on the

total abundance of N_2 (McElroy et al 1977). Table 4 summarizes current estimates of the volatile abundances of Venus, Earth, and Mars (Pollack & Black 1979). Also given are values appropriate for two classes of meteorites and the Sun, which, however, refer to the bulk content of these objects.

Several attempts were made to estimate the "unseen" components of the Martian volatile inventory on the basis of the Viking results at a time when the Venus results had not yet been obtained. In essence, each of these studies selected one of the components of the Martian volatile inventory that was known, and determined the remaining components by appropriately scaling the volatile inventory of the Earth or a class of meteorites, which was assumed to have the same *relative proportion* of volatiles as Mars. Rasool & LeSergeant (1977) used the Martian ^{36}Ar abundance and LL chondrites for this purpose, with the meteoritic material forming a 100-km thick veneer. Although they concluded that this model was consistent with the Earth's volatile inventory, more recent comparisons by Bogard & Gibson (1978) indicate that the $^{36}\text{Ar}/\text{C}$ ratio of LL chondrites, as well as other classes of chondrites, differs substantially from the terrestrial value, and hence scaling on the basis of ^{36}Ar can be dangerous (see Table 4). Anders & Owen (1977) also favored a veneer source, due either to inhomogeneous accretion or to asteroidal/cometary sources, but they considered a carbonaceous chondrite of type 3V to be a more appropriate analogue. They also employed a very sophisticated model in which elements are divided into five volatility classes, with ^{36}Ar belonging to the class of highest volatility and ^{40}Ar , since it is derived from the decay of ^{40}K , belonging to the class of second highest volatility. According to them, the higher value of $^{40}\text{Ar}/^{36}\text{Ar}$ for the Martian atmosphere, as compared to the Earth's, indicates that Mars was more poorly endowed with volatiles than the Earth. The analysis of Owen & Anders is subject to the same criticism as that of Rasool & LeSergeant. Clark & Baird (1979) have used the Martian value of ^{40}Ar in conjunction with the relative abundances of the Earth's volatile inventory to estimate other components of the Martian volatile inventory. The chief weakness with this approach is that ^{40}Ar is built up in the interior only gradually with time and thus its atmospheric abundance depends chiefly on outgassing events that occurred after planetary differentiation, whereas all the other volatiles can be released into the atmosphere chiefly at earlier epochs (see Table 2). Finally, McElroy et al (1977) used their estimate of the N_2 abundance, inferred from the $^{15}\text{N}/^{14}\text{N}$ ratio, together with terrestrial volatile abundances, to infer the amount of CO_2 and H_2O in the Martian volatile inventory. These amounts were consistent with the lower bound of 1 bar of oxygen in the form of either CO_2 or H_2O , as

Table 4 Volatile abundances (gm/gm) and isotopic ratios^a

Object	Primordial Ar	N ₂	CO ₂	H ₂ O	⁴⁰ Ar/ ³⁶ Ar	²⁰ Ne/ ³⁶ Ar	⁸⁴ Kr/ ³⁶ Ar	³⁶ Ar/ ¹⁴ N	¹⁵ N/ ¹⁴ N	N/C
Venus	6 × 10 ⁻¹⁰ to 9 × 10 ⁻⁹	(2.0-2.2) × 10 ⁻⁶	(9.4-9.6) × 10 ⁻⁵	1 × 10 ⁻⁹ to 6 × 10 ⁻⁸	1.1 to 1.3	0.2 to 0.8	0.005 to 0.015	8 × 10 ⁻⁵ to 9 × 10 ⁻⁴	2.6 × 10 ⁻³ to 4.6 × 10 ⁻³	0.05 to 0.09
Earth	4.6 × 10 ⁻¹¹	2.4 × 10 ⁻⁶	1.6 × 10 ⁻⁴	2.8 × 10 ⁻⁴	292	0.5	0.036	5 × 10 ⁻⁶	3.6 × 10 ⁻³	0.05
Mars	(1.9-2.5) × 10 ⁻¹³	4 × 10 ⁻⁸ to 4 × 10 ⁻⁷	> 3.5 × 10 ⁻⁸	> 5 × 10 ⁻⁶	2500 to 3500	0.2 to 0.9	0.01 to 0.05	2 × 10 ⁻⁷ to 2 × 10 ⁻⁶	5.6 × 10 ⁻³ to 6.6 × 10 ⁻³	—
Ordinary chondrites	3 × 10 ⁻¹² to 1 × 10 ⁻⁹	—	—	—	—	~0.2	0.015 to 0.029	1 × 10 ⁻⁷ to 7 × 10 ⁻⁷	—	0.01 to 0.05
Carbonaceous chondrites	4 × 10 ⁻¹⁰ to 1 × 10 ⁻⁹	—	—	—	—	~0.2	0.015 to 0.029	1 × 10 ⁻⁷ to 7 × 10 ⁻⁷	—	0.01 to 0.05
Sun	1 × 10 ⁻⁴	1.3 × 10 ⁻³	1.3 × 10 ⁻²	9.5 × 10 ⁻³	—	31	0.00027	2.7 × 10 ⁻²	—	0.31

^a Adapted from Pollack & Black (1979).

implied by an essentially identical $^{18}\text{O}/^{16}\text{O}$ ratio for the Earth and Mars (McElroy et al 1977). McElroy et al also noted that their approach implied that the relative proportions of rare gases and other volatiles, such as N_2 , were different for the two planets. As discussed next, the Venus data support these conclusions.

Pollack & Black (1979) made use of the new Venus data, in conjunction with the volatile abundances for the other objects listed in Table 4, to draw tentative conclusions about the origin of the atmosphere of the outer three terrestrial planets. In accord with Table 4, they noted four key trends: 1. the absolute abundances of N_2 and CO_2 are essentially the same for Venus and the Earth, but Mars has a lower abundance of N_2 (absolute abundance means the ratio of the mass of a given volatile to that of the planet); 2. the absolute abundance of ^{36}Ar and the ratio $^{36}\text{Ar}/^{14}\text{N}$ decrease systematically by several orders of magnitude from Venus to the Earth to Mars; 3. a similar sharp increase occurs for $^{40}\text{Ar}/^{36}\text{Ar}$; and 4. the ratios of *primordial* rare gas species (e.g. $^{20}\text{Ne}/^{36}\text{Ar}$) are very similar for the terrestrial planets and chondritic meteorites, but differ considerably from solar values. Sources involving the solar nebula and solar wind are inconsistent with trend 4, while the one involving meteorites and comets is incompatible with trends 1 and 2. The release of intrinsic volatiles can account for all these trends, if one assumes that volatiles were incorporated into the planet-forming material at times when there were large pressure differences among the regions where Venus, the Earth, and Mars were forming, but little temperature differences. These constraints on conditions in the solar nebula follow from the differences in the mode of incorporation of rare gases and other volatiles into planet-forming material, as discussed in the previous section. Rare gases are occluded, but C, N, and H_2O are incorporated into chemical compounds. Hence, the amount of rare gases incorporated per gram of other volatiles increases linearly with pressure and decreases exponentially with temperature. Also, the ratio of one incorporated rare gas species to a second varies with temperature. Hence, trend 4 implies a nearly constant temperature, while trend 2 implies a strong pressure gradient. Note that these conditions need not occur simultaneously, but rather apply to whenever volatiles were formed in different regions. Whether such conditions are physically realizable needs to be carefully assessed. This conclusion that the atmospheres of the three terrestrial planets are derived from the release of intrinsic volatiles is consistent with the rough estimates of source strengths given in the previous section.

Pollack & Black (1979) were able to quantitatively fit all the data of Table 4 with a model that allowed for differences among the three planets in nebular pressure and differences in the efficiency of the release of

volatiles at the times of accretion and interior differentiation and at later times. Note again that little ^{40}Ar comes out during the early epochs of outgassing. If P , e_1 , and e_2 represent nebular pressure and efficiency of outgassing for the early and later epochs, all normalized to a value of 1 for the Earth, they find $P = 20 \rightarrow 200$, $e_1 = 1$, and $e_2 = 1/15 \rightarrow 1/1.5$ for Venus and $P = 1/40 \rightarrow 1/20$, $e_1 = 1/5 \rightarrow 1/20$, and $e_2 = 1/20$ for Mars. These estimates of e_1 and e_2 implicitly assume that Venus, the Earth, and Mars were all endowed with the same proportion of N_2 - and CO_2 -forming volatiles. If not, e_1 and e_2 must include differences in initial abundances as well as differences in outgassing efficiency.

Information on bulk potassium content, crustal potassium content, and rare gas abundances in rocks allows us to place some further constraints on the efficiency of volatile release. The bulk K content of the Moon is about a factor of 2 smaller than that of the Earth, as inferred from surface heat flow measurements and K/U and K/Th ratios in rocks for these two bodies (Anders & Owen 1977). If the global abundance of K for Mars lies intermediate between that of the Earth and Moon, then differences in volatile endowment can account for no more than a factor of 1/2 in the value of e_2 for Mars and, thus, this low value is chiefly due to a much more incomplete outgassing of ^{40}Ar from the Martian interior.

The above small spread in values of bulk K content implies that sizeable variances in crustal K abundances may provide a qualitative guide to the efficiency of volatile release, with more highly differentiated objects presumably having higher efficiencies. The crustal K abundances of the Earth and Venus are quite similar, that of Mars is about a factor of 4 smaller, and that of the Moon about a factor of 20 smaller than the terrestrial value (Anders & Owen 1977). Hence, comparable release efficiencies are expected for the Earth and Venus, with progressively smaller values for Mars and the Moon. This expectation is consistent with the above estimates of the relative efficiency factors e_1 and e_2 .

The absolute efficiency of later volatile release for the Earth can be obtained from comparisons of bulk K content and atmospheric ^{40}Ar abundance. Values ranging from 25% (Hart et al 1979) to 50% (Stacey 1979) have been obtained in this manner, with the spread in values reflecting differing treatments of mantle heat transport and differing assumptions on the similarity of the K/U and K/Th ratios for the crust and mantle. Rocks derived from the upper mantle of the Earth (≤ 400 km) have very high $^{40}\text{Ar}/^{36}\text{Ar}$ ratios ($\sim 10^4$) compared to the atmospheric value (~ 300) and low absolute abundances of ^{36}Ar , while rocks derived from deeper depths have $^{40}\text{Ar}/^{36}\text{Ar}$ ratios (~ 450) similar to the atmospheric value and much higher absolute abundances of ^{36}Ar (Stacey

1979). These results imply that the absolute efficiency for outgassing primordial rare gases is greater than that for ^{40}Ar ; that the Earth has incompletely outgassed both types of rare gases; and that its initial endowment of volatiles extended to sizeable depths in the mantle, perhaps encompassing the entire mantle.

Earth

Here, we consider controls on the present composition of the Earth's atmosphere, its long term evolution, and the ability of the early atmosphere to generate an enhanced greenhouse effect and hence counteract the lower solar luminosity then. In discussing the present and past atmospheres of the Earth, we will concentrate on water vapor, hydrogen, oxygen, ozone, and carbon-, nitrogen-, and sulfur-containing gases. Table 1 summarizes the concentration of these species in the Earth's current, highly oxidizing atmosphere. The dominant C, N, and S species are CO_2 , N_2 , SO_2 , and H_2S .

As discussed in the previous section, the amount of atmospheric water vapor is buffered by the huge ocean reservoir, with the H_2O concentration in the troposphere being limited by its saturation vapor pressure at ambient temperature and its concentration at higher altitudes being regulated by the tropopause cold trap. However, the very efficient removal of water vapor from the troposphere by condensation and precipitation keeps the time-averaged relative humidity somewhat below unity (Rossow 1978). The biosphere converts nitrogen into such "fixed" compounds as nitrates, but it also efficiently recycles fixed nitrogen back into the atmosphere as N_2 and N_2O (Holland 1978a). As a result, much of the N of the Earth's volatile inventory is present as atmospheric N_2 rather than as subsurface nitrate. The biosphere is also responsible for the trace amounts of CH_4 , NH_3 , and H_2S in the atmosphere, despite the large amount of free O_2 (Walker 1977). Photodissociation of these gases and water vapor in the upper atmosphere helps to generate H_2 . The very low abundance of S-containing gases is due to the photochemical conversion of H_2S to SO_2 and the efficient removal of SO_2 by dissolution in water cloud particles and their subsequent precipitation and by sulfate aerosol formation. Finally, the trace amount of ozone in the atmosphere is ultimately governed by the oxygen abundance through a complex set of photochemical reactions (Logan et al 1978).

The amounts of CO_2 and O_2 in the present atmosphere are thought to be governed by complex geochemical cycles that involve the transfer of C and O compounds between the atmosphere and subsurface rock reservoirs (Walker 1977, Holland 1978a). The carbon cycle is illustrated in Figure 5a (Walker 1977). The primary reservoir is the crustal rocks,

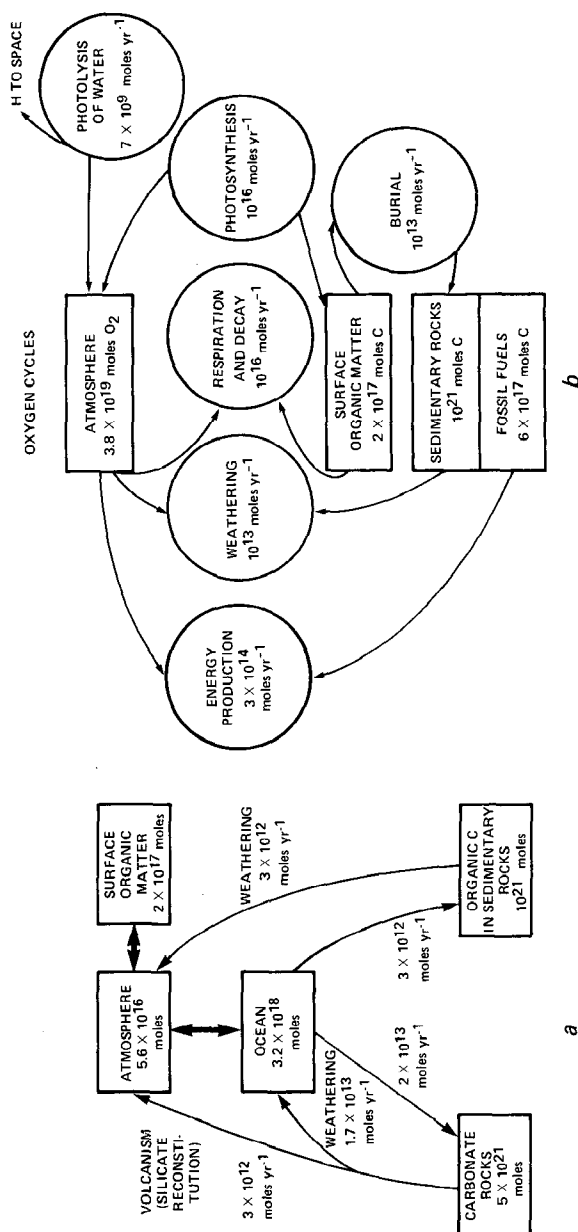


Figure 5 Geochemical cycles of carbon (a) and oxygen (b). The rectangular boxes show the amount of material stored in major reservoirs, while the numbers within circles in (b) and along arrows in (a) indicate the fluxes between reservoirs. From Walker (1977).

with the oxidized C-containing rock reservoir, i.e. carbonate rocks, being substantially larger than the reduced C (organic) rock reservoir. Conceivably, the atmospheric CO_2 content is determined by a dynamic equilibrium between the loss of CO_2 through the weathering of silicate rocks to carbonate rocks and the addition of CO_2 due to the metamorphism of buried carbonate rocks and the outgassing of the resulting CO_2 (Walker 1977) as well as possibly juvenile CO_2 (Holland 1978a). The amount of CO_2 lost by weathering probably varies monotonically with the atmospheric partial pressure, but in a rather complicated way (Walker 1977): First, cations must be extracted from silicate rocks by rainwater containing dissolved CO_2 and then the CO_3^{2-} anion content of seawater must be high enough for the cations to precipitate in the sea as carbonates. At present, almost all the Ca leached from silicate rocks is precipitated as calcite, with this being the dominant carbonate rock. At higher partial pressures of CO_2 , other carbonates may be produced in abundant amounts [e.g. $\text{CaMg}(\text{CO}_3)_2$] and, at lower pressures, not all of the leached Ca^{2+} may be precipitated as calcite (Holland 1978a).

Figure 5*b* illustrates the oxygen cycle (Walker 1977). As for the C cycle, subsurface rocks constitute the largest reservoir and the amount of atmospheric O_2 may be determined by a dynamic equilibrium between the rate at which O_2 is being added to and lost from the atmosphere. The principle source is the tiny fraction ($\sim 0.1\%$) of organic matter produced by photosynthesis that is buried in sea sediments without being oxidized. The dominant contributor to this net source of O_2 is organic matter produced in the sea by phytoplankton. The O_2 generated in this manner constitutes a source that is a thousand times more potent than the source due to water photolysis followed by the escape to space of H. Oxygen is lost from the atmosphere as the result of the chemical weathering of rocks containing reduced compounds, with old organic sediments constituting the dominant sink material. Almost complete oxidation occurs during chemical weathering. Hence, control on the O_2 level in the atmosphere is exerted through the dependence of the photosynthetic source on the O_2 partial pressure. For example, increasing this pressure causes an increase in the amount of O_2 dissolved in seawater and a reduction in the fraction of buried organic matter that is not oxidized.

We next discuss the early atmosphere of the Earth and its evolution to its present state. Our previous discussion of thermal history models indicated that much of the release of volatiles occurred during the earliest epochs ($\sim 1 \times 10^9$ years), in conjunction with accretion and global internal differentiation. Later degassing of the remaining juvenile volatiles may have occurred episodically throughout the Earth's history in conjunction with more localized volcanism. A rather key feature in the history of the

Earth's volatiles is the extensive recycling of them between the atmosphere and subsurface, as illustrated in Figure 5. On the basis of the size of the dominant C reservoirs and the fluxes to them given in Figure 5a, we estimate a characteristic recycling time of about 3×10^8 years.

The above history of volatile release implies that sizeable oceans were present over almost all of the Earth's lifetime. As at present, atmospheric water vapor in the past was buffered by the oceans, with its abundance being a sensitive function of surface temperature.

Upper bounds can be placed on the amount of solar nebular derived H_2 present in the earliest atmosphere. Using the present amount of atmospheric neon and solar elemental abundances, Walker (1977) shows that the H_2 pressure could have been no more than about 10^{-1} bars. Quite likely it was much less since most of the terrestrial neon was derived from gases trapped in planet-forming material.

After the solar nebula was dissipated, the fractional abundance of hydrogen by number, f_{H_2} , was controlled by a balance between its rate of release from accretional and interior sources and the escape rate of H from the top of the atmosphere. If we assume that the exospheric temperature T_{ex} exceeded 500 K, as it does today ($T_{ex} \sim 1500$ K), the escape rate is equal to the diffusion limiting flux, as given by Equation (2). To obtain a very crude estimate of the initial rate of release of H_2 , we suppose that half of the juvenile volatiles were released during the first 3×10^8 years and that $H_2/H_2O = 0.1$ in the released gases, a value intermediate between ones appropriate for silicate melts containing metallic iron and ones containing only FeO and Fe_2O_3 in their present proportions (Holland 1962). Equating the release and escape rates of H_2 , we find $f_{H_2} \cong 10^{-3}$. Thus, the partial pressure of H_2 was $\sim 10^{-3}$ bars during this initial phase, if the total pressure was comparable to its present value.

Recycling of water through the Earth's interior at the current characteristic time scale for C compounds would result in a similar mixing ratio and partial pressure of H_2 throughout subsequent epochs, until the time that significant amounts of free oxygen began to accumulate in the atmosphere. Even higher H_2 amounts could have been realized at the earliest times as a result of metallic iron being present in the melt and/or a possibly much shorter time scale associated with the accretional formation of the Earth.

It is very difficult to estimate the oxidation state of the C-, N-, and S-containing gases in the Earth's early atmosphere. For the full range of possible oxidation states of iron, the released volatiles contained only trace amounts of CH_4 and NH_3 , with CO, CO_2 , N_2 , and H_2S representing the dominant C, N, and S species (Holland 1962). For the higher oxidation states of iron, sizeable, even dominant amounts of SO_2 were

released. Thus, significant amounts of CH_4 and NH_3 could have resulted only from the hydrogenation of the more oxidized forms of these compounds, once the latter had been placed in the atmosphere. From the standpoint of thermodynamic equilibrium, a sizeable conversion of N_2 to NH_3 and a complete reduction of CO and CO_2 to CH_4 were favored by the comparatively low atmospheric temperature (~ 300 K) and moderate H_2 partial pressure ($\sim 10^{-3}$ bars; Figure 2).

However, the degree to which thermodynamic equilibrium was approached may have been limited by both the very slow reaction rates, especially for NH_3 , and by the total amount of H_2 available. With regard to the latter, H_2/CO and H_2/CO_2 ratios of at least 3/1 and 4/1, respectively, are required to fully reduce these gases to CH_4 . But $\text{H}_2\text{O}/\text{CO}_2 \cong 5$ in the Earth's volatile inventory (Table 4). Hence, either $\text{H}_2/\text{H}_2\text{O}$ had to approach the value appropriate for a metallic iron-containing melt or water had to be preferentially recycled to meet the above stoichiometric constraints on complete reduction.

It has been traditional to attempt to constrain the oxidation state of the Earth's early atmosphere by the requirement that it favor the generation of complex organic compounds, ones capable of leading to the origin of life. As there is evidence for living organisms in the geological record over at least the last 3 billion years (Windley 1977), the origin of life presumably occurred during the first billion years of the Earth's history. Early experiments by Miller and Urey showed that complex organic molecules, including a variety of amino acids, are produced when a highly reduced atmosphere, dominated by NH_3 , CH_4 , H_2 , and H_2O , is subjected to electrical discharges (Miller & Orgel 1974). Subsequent experimentation has yielded comparable results for a variety of energy sources, including UV light, and for less reducing mixtures of gases (Miller & Orgel 1974). However, in all cases, reducing gases have constituted a significant fraction of the starting materials and it has been necessary to quickly remove the organic molecules from the energy source in order to preserve their integrity.

Theoretical calculations by Pinto et al (1979) suggest that at least formaldehyde can be produced in copious amounts in an atmosphere that is only mildly reducing. In these calculations, the atmosphere was assumed to have its present abundance of N_2 , H_2O , and CO_2 , with only trace amounts of H_2 ($\sim 10^{-3}$ bars) and CO ($\sim 10^{-6}$ bars) being present. The H_2 abundance is consistent with the estimates given above, while the CO amount is determined by CO_2 and H_2O photochemistry. Formaldehyde is generated through a series of photochemical reactions in which either H_2 or CO are the ultimate reducing agents. According to the model calculations, about 1% of the formaldehyde reaches the ocean

before being destroyed by UV sunlight. Pinto et al (1979) find that the net production rate is adequate to generate a 10^{-2} molar concentration of CH_2O in the ocean in $\sim 10^8$ years. Whether more complicated organic molecules would result is unclear. Baur (1978) has even suggested that organic molecules could be produced in an atmosphere containing no reducing gases, with Fe^{2+} -containing clays acting as the reducing agent. In any event, few constraints on the CH_4 and NH_3 content of the early atmosphere appear to be placed by our current understanding of chemical steps leading to the origin of life.

Due to changes in outgassing, photochemical conversion processes, and photosynthesis by green plants, the atmosphere became more oxidizing with increasing time. The early disappearance of metallic iron and the subsequent progressive oxidation of interior Fe by biologically produced O_2 caused the $\text{H}_2/\text{H}_2\text{O}$ ratio in volcanic effluent to change from about 1 to its present value of about 10^{-2} . Also, a decline in the interior heat flux by about a factor of 3 over the age of the Earth may have led to a decline in the outgassing rate (Holland 1978b). The above changes resulted in a decrease in the mixing ratios of H_2 , NH_3 , and CH_4 .

Photodissociation by UV radiation at wavelengths less than about $0.23\ \mu\text{m}$ converts NH_3 very efficiently into N_2 (Kuhn & Atreya 1979). For example, with f_{NH_3} maintained at 10^{-5} or higher, the current atmospheric amount of N_2 can be photolytically generated from NH_3 in only 10^7 years in an atmosphere containing only N-gas species (Kuhn & Atreya 1979). This rapid destruction of NH_3 may be slowed down by the presence of H_2 in the atmosphere and by the presence of H_2O in the upper atmosphere. Water absorbs in the same range of UV wavelengths as NH_3 (Brinkmann 1969). Conceivably the NH_3 abundance in the upper troposphere and higher atmosphere may be greatly reduced due to its reaction with H_2S to form NH_4SH clouds in the upper troposphere, by analogy to the cloud layers of the giant planets (Weidenschilling & Lewis 1973).

Photolysis may also tend to destroy the CH_4 component of the atmosphere. Photochemical reactions create minor amounts of hydrocarbons in the upper atmosphere (Lasaga et al 1971). The higher order hydrocarbons may polymerize and hence form hydrocarbon aerosols that are quickly removed from the atmosphere to form an "oil slick" at the ocean interface. Lasaga et al (1971) estimate that a 1-bar atmosphere of CH_4 would be totally polymerized in only 10^6 to 10^7 years. Conceivably, much longer time scales may apply when allowance is made for the presence of some H_2 and for the thermal decomposition of the polymers.

Not even N_2 is "safe" in a primitive atmosphere. Lightning and subsequent photochemistry can convert the current atmospheric amount of

N_2 in about 5×10^8 years into nitrates, which dissolve in the oceans (Yung & McElroy 1979).

Due to buffering by Fe and FeO, only negligible amounts of O_2 are contained in volcanic effluents. Furthermore, the O_2 generated from the photodissociation of H_2O and the subsequent escape of H is completely removed by the reducing gases emanating from the interior. The escape rate of H resulting from H_2O photodissociation is controlled by diffusion (Hunten & Donahue 1976). For H_2O mixing ratios in the stratosphere comparable to today's value, the photolytic production of O_2 is limited to a rate of about 5×10^7 molecules/ cm^2/s . This production rate is about two orders of magnitude smaller than the volcanic input of H_2 given above for the early Earth. Even the current volcanic input of reducing gases is probably sufficient to overwhelm the production of O_2 from water (Kasting & Donahue 1979).

Thus, the introduction of nontrivial quantities of O_2 into the Earth's atmosphere awaited the development of the first green plants capable of photosynthesizing CO_2 and H_2O into organic matter and releasing O_2 as a waste product. Studies of the geological record suggest that the first oxygen-producing organisms appeared about 2.3×10^9 years ago and were similar to blue-green algae of today (Windley 1977).

However, the buildup of atmospheric oxygen may have been delayed somewhat after the first appearance of O_2 -producing organisms by the oxidation of reduced compounds in seawater, such as FeO. It has been suggested that this oxidation process generated the prominent banded iron formations of the epoch centered around 2.1×10^9 years ago (Cloud 1972). The delay in the buildup of atmospheric O_2 may have given biota time to evolve oxygen-mediating enzymes that permitted the safe handling and eventual utilization of the otherwise poisonous O_2 . Prior to 2×10^9 years ago, the occurrence of reduced minerals of uranium and iron suggests that the atmospheric O_2 partial pressure was quite low (Holland 1978b). However, subsequently, the widespread occurrence of red beds—ferric oxide containing sediments that were formed *on land*—suggests a buildup in the O_2 pressure.

During much of the Earth's history, all lifeforms were single-celled organisms called prokaryotes. Their cells lacked internal organelles, such as a nucleus. The first microscopic forms of life with intracellular organelles—eukaryotes—appeared about 1.4×10^9 years ago (Windley 1977). Their more sophisticated cell organization permitted the occurrence of multicellular organisms. This key evolutionary development may be related to the buildup of atmospheric O_2 : almost all current-day eukaryotes are capable of respiration, i.e. the utilization of O_2 for the metabolic release of energy. Furthermore, current-day microorganisms switch from

fermentation to respiration when the oxygen partial pressure exceeds 1 % of the present atmospheric level (PAL). Thus, the first occurrence of eukaryotes may coincide with the time when the atmospheric O_2 level reached 1 % PAL. The replacement of fermentation by respiration permitted organisms to obtain a much larger energy release during metabolism.

Further buildup in the oxygen level may have encouraged the development of more sophisticated means of handling respiration, including the advent of highly specialized systems, such as early versions of the respiratory, circulatory, and nervous systems. The first megascopic forms of life appeared about 7×10^8 years ago (Windley 1977).

The increase in atmospheric oxygen content also led to an increase in atmospheric ozone, which more and more effectively prevented potentially lethal UV radiation from reaching the surface (Berkner & Marshall 1965, Kasting & Donahue 1979). This buildup of atmospheric ozone may have permitted certain organisms to live near the top of the oceans and set the stage for the invasion of the continents by plants about 4×10^8 years ago (Berkner & Marshall 1965). Unfortunately, there is inadequate information on the doses of UV radiation that can be tolerated by various organisms, and hence it is difficult to define at present critical ozone levels and hence critical oxygen levels (L. Margulis, private communication).

Carbonate rocks are present throughout the geological record, which spans the last 3.8×10^9 years (Windley 1977). Hence, some atmospheric CO_2 existed over this entire period. Calcite— $CaCO_3$ —is the dominant constituent of carbonate sediments formed during recent times. However, there is some evidence that increasing amounts of dolomite— $CaMg(CO_3)_2$ —are present in progressively older carbonate sediments (Holland 1978b). This trend may be related to a higher heat flux and hence a higher outgassing rate in the past, which could imply a higher atmospheric CO_2 amount in the past (Holland 1978b). However, the absence of significant amounts of Na- and K-containing carbonates in the geological record probably implies that the CO_2 partial pressure was always less than $\sim 10^{-1}$ bars over the last 3.8×10^9 years (H. D. Holland, private communication).

Finally, we consider attempts to reconcile the lower solar luminosity in the past with the occurrence of moderate surface temperatures then, as implied by the occurrence of life and oceans for at least the last 3.8×10^9 years (Sagan & Mullen 1972). Greenhouse calculations indicate that the average surface temperature would have fallen below the freezing point of seawater about 2×10^9 years ago if the atmospheric composition and mass were the same then as today (Sagan & Mullen 1972). Hence, the

atmosphere must have been different then. Sagan & Mullen considered two types of modified atmospheres, which can produce large enough greenhouse effects to successfully counteract the trend in the solar luminosity. One involved an atmosphere nearly the same as today's, but with NH_3 also present at the level of several parts per million. The other involved the first modified atmosphere plus 1 bar of H_2 . Hart (1978) constructed evolutionary models of the Earth's atmosphere, with a large number of adjustable parameters. He successfully overcame the solar luminosity problem with a model in which the CO_2 pressure steadily declined with time, CO_2 was always the dominant C-gas species, and small amounts of NH_3 were present for the first 2×10^9 years. Subsequently, Owen et al (1979) performed much better greenhouse calculations with Hart's prescribed CO_2 time history and found that adequate greenhouse effects occurred at all times with only CO_2 and H_2O opacity, due to the occurrence of larger amounts of CO_2 at earlier times.

It is of interest to compare the above greenhouse models with the discussion given earlier in this subsection of the evolutionary history of the Earth's atmosphere. Even during earliest times, hydrogen escapes too rapidly for it to ever become the dominant constituent of the atmosphere, and hence Sagan & Mullen's H_2 -rich atmosphere seems implausible. The occurrence of small amounts of NH_3 during the first several billion years, as invoked in their other model and Hart's model, is not unreasonable, but the rapid photolytic destruction of NH_3 presents a potentially serious problem. The steadily increasing amounts of CO_2 with time into the past, called for in the Owen et al and Hart models, is not inconsistent with our understanding of the CO_2 geochemical cycle, as explained above, but more work is needed on this subject.

Mars

In this section, we discuss the evolution of the mass and composition of the Martian atmosphere and the atmospheric and climatic changes involved in generating its fluvial channels and polar layered terrain. According to Pollack & Black's (1979) model for the origin of the atmospheres of the terrestrial planets, approximately 1–3 bars of CO_2 (or equivalently 0.3–1 bars of CH_4), 50–100 mb of N_2 (or NH_3), and an equivalent depth of 80–160 meters of water have been outgassed from the interior of Mars over the planet's lifetime. If Mars has the same proportion of volatiles as the Earth, the above figures represent no more than 20% of the planet's total volatile content. The inefficient degassing of Mars, as compared to that of the Earth ($e_1 \lesssim 1/5$), may be due to a combination of a smaller amount of accretional heating and a smaller energy release per unit mass during core formation, with both of these

differences arising from Mars' smaller mass relative to that of the Earth. According to Figure 1 and Pollack & Black's model, a large fraction of the total degassing took place over the first billion or so years of history, during the period of accretion and global internal differentiation. However, significant additional degassing (~ 20 – 50% of the total) took place at later times in association with major volcanic events. These volcanic events are spread over much of Martian history, with perhaps a decline occurring during the last billion years due to a thickening of the lithosphere (Toksöz et al 1978). Thus, the present degassing rate is expected to be substantially smaller than the time-averaged value, in accord with McElroy et al's (1977) estimate that it is at least a factor of 20 times smaller than the average value on the basis of evolutionary models of the $^{15}\text{N}/^{14}\text{N}$ ratio.

We next consider the evolution of the oxidation state of the atmosphere. Following the same type of analysis as for the Earth, we estimate that during the early phase of volatile release $f_{\text{H}_2} \cong 10^{-3}$, with this mixing ratio declining at subsequent times towards its current value of 4×10^{-6} . The current mixing ratio of hydrogen is due entirely to H_2O dissociation. Once again, it is very difficult to estimate the state of oxidation of C and N compounds in Mars' early atmosphere, with there being some possibility of significant proportions of CH_4 and NH_3 in addition to CO_2 and N_2 .

Photochemical processes may have greatly reduced the CH_4 and NH_3 contents of the early partially reducing atmospheres and eventually led to the current atmosphere that contains only CO_2 and N_2 . As discussed in the subsection on the Earth, photochemical conversion of NH_3 to N_2 can occur so rapidly as to thwart the establishment of thermodynamic equilibrium concentrations of NH_3 . Also, creation of higher hydrocarbons from methane acts as a sink for CH_4 since the higher hydrocarbons can drop out of the atmosphere and collect at the surface. According to calculations by Yung & Pinto (1978), a 1-bar atmosphere of CH_4 could be lost in this way in only about 10^8 years. Once this occurs, oxygen generated from the photodissociation of water vapor and the escape of H oxidizes the hydrocarbons, eventually resulting in the production of a CO_2 atmosphere on a time scale of 10^8 – 10^9 years (Yung & Pinto 1978). While the eventual production of a CO_2 , N_2 atmosphere seems to be well established, the reader is again cautioned that additional work is needed before the stability of CH_4 - and NH_3 -containing atmospheres is adequately understood.

Through a series of loss processes, almost all of the outgassed volatiles have been removed from the atmosphere. At the low temperatures on Mars, saturation and condensation hold the water vapor content of the atmosphere to a very low level ($\sim 10^{-5}$ m). Principal near-surface

reservoirs of water include the fine-grained regolith, subsurface permafrost layers, and the polar layered terrain, with probably only small amounts being present in the permanent polar caps (Pollack 1979). According to Clark & Baird (1979), the fine-grained regolith may have removed atmospheric water through the irreversible formation of clays and salts, the reversible hydration of salts, and reversible adsorption, with a net removal of perhaps as much as several tens of meters of water. Under present conditions, subsurface permafrost *in contact with the atmosphere* is stable down to a latitude of about 40° (Toon et al 1979). A modest amount of water (~ 3 m) has been lost over Mars' lifetime due to the joint escape of H and O from the top of the atmosphere (McElroy 1972), with the H escaping by thermal evaporation and the oxygen by photochemical escape. In fact, the coupling of these processes through the interaction of O_2 and H_2 in the lower atmosphere insures that at present precisely two H escape for every O lost (McElroy 1972).

While CO_2 is the dominant constituent of Mars' present atmosphere, a much larger amount of CO_2 (1–3 bars) resides in near-surface reservoirs. At one time, it was thought that the *permanent* polar caps of Mars might be made of CO_2 and contain large amounts of CO_2 ice. However, Viking data show that the northern cap is made of H_2O ice, while the southern cap might contain CO_2 , at least during some years, but probably not a large amount (Kieffer et al 1977). The two major sinks for CO_2 are thought to be reversible adsorption onto the fine-grained regolith and the irreversible formation of carbonate rocks. According to Fanale & Cannon (1979), the regolith may at present contain 20 times as much CO_2 as the atmosphere, i.e. 100 mb. The loss of CO_2 from the atmosphere to these reservoirs may have occurred gradually over the course of time, as weathering produced carbonate rocks and a progressively deeper regolith and as the regolith was moved preferentially towards the colder subpolar regions. Thus, at earlier times, the pressure may have been much larger. Finally, through a combination of photochemical escape and solar wind sweeping, Mars has lost an amount of CO_2 comparable to that currently residing in the atmosphere (McElroy 1972).

Nitrogen has also been gradually lost from the atmosphere due mostly to the photochemical formation of HNO_2 and HNO_3 , which reacted with surface minerals to form nitrates. Also, some N_2 (1–2 mb) has been lost by photochemical escape (McElroy et al 1977). Settle (1979) has studied the fate of sulfur gases (H_2S and SO_2) vented into the atmosphere. He finds that on a time scale of a few years, under current conditions, these gases are converted to sulfuric acid aerosols, which are subsequently removed from the atmosphere by scavenging and sedimentation. The acid reacts with surface minerals to produce sulfate salts.

The surface of Mars has been excised by a number of channels, whose morphology suggests that they were formed by running water. Some classes of these fluvial channels, particularly the numerous gullies, appear to require surface temperatures above the freezing point of water for their formation, although others, particularly the large outflow channels, might be formed under current Martian climatic conditions (Pollack 1979). The gullies were probably formed after the end of the first two stages of volatile release and towards the beginning of the third stage, i.e. several billion years ago (Pollack 1979). At first glance, it is a rather remarkable inference that clement conditions existed on Mars several billion years ago, in view of its current cold climate and a lower solar luminosity then.

Attempts have been made to explain the clement conditions needed for channel formation by invoking atmospheres capable of generating a large greenhouse effect. Within this context, Pollack (1979) has studied fully reducing atmospheres, with NH_3 , H_2O , CH_4 , and H_2 as the sources of infrared opacity; Sagan (1978) has examined mildly and very reducing atmospheres, with CO_2 , NH_3 , H_2 , and H_2O opacity sources; and Pollack (1979) and Cess et al (1979) have investigated fully oxidized atmospheres, with CO_2 and H_2O opacity sources. Figures 6*a* and *b* illustrate Pollack's results for fully oxidized and reduced atmospheres, respectively. In Figure 6*a*, curves of surface temperature are displayed as a function of insolation factor f for fixed values of surface pressure P . The horizontal line indicates the melting temperature of water ice. The parameter f is defined as the ratio of the actual solar energy absorbed to the globally averaged amount of insolation that is currently being absorbed by Mars at its mean distance from the Sun. The value of f depends on the solar luminosity, the eccentricity, and orbital position of Mars at the time of interest, and the geographical position of interest (Pollack 1979). For simplicity, consider an orbital position close to perihelion when Mars had a large eccentricity value (see below). Then the orbital factors offset the lower solar luminosity several billion years ago and $f \cong 1$. In this case, a surface pressure of about 2 bars is required to reach the melting point of water for CO_2 - H_2O atmospheres according to Figure 6*a*. More precise calculations by Cess et al (1979) suggest a "critical" pressure of 1 bar. Values of the "critical" pressure for other situations, that imply other values of f , are given in Pollack (1979). Thus, the fully oxidized models require that most of the CO_2 outgassed by Mars be present in the atmosphere to generate the required greenhouse effect. This condition is not unreasonable in light of the earlier discussion of the evolution of the surface pressure, but whether the surface reservoirs were sufficiently underdeveloped at this earlier time is still an open question. It is interesting to note that the very conditions that permitted a strong greenhouse effect

may have led to its demise through a much enhanced rate of regolith and carbonate rock formation at times when liquid water was available (Pollack 1979).

Figure 6*b* shows corresponding greenhouse calculations for fully reduced atmospheres having varying proportions of NH_3 and H_2 , with CH_4 being the principal gas and NH_3 and H_2 having mixing ratios of 0.03 and 0.1 in the nominal case. For all the curves, $f = 1$. These calculations indicate that H_2 opacity is unimportant, but NH_3 opacity is very important. These fully reduced atmospheres provide the needed greenhouse effect with total pressures not in excess of the amount of out-gassed C gases ($\text{CH}_4 \lesssim 1$ bar) only when nonnegligible amounts of NH_3 are present. Thus, it is necessary to find a way of preventing the rapid photolytic destruction of NH_3 , if they are to be viable options. Sagan (1978) required about 1 bar of CO_2 and an ammonia mixing ratio of about $10^{-4.5}$ to generate the required surface warming with his mildly reducing atmospheres, with $f \cong 0.8$. Again, the stability of NH_3 could constitute a serious problem.

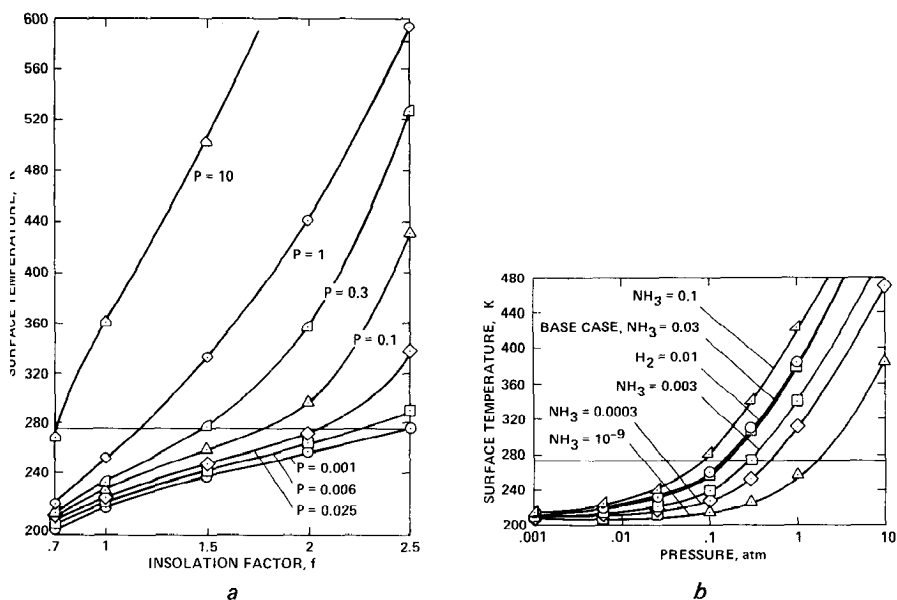


Figure 6 (a) Surface temperature of Mars as a function of insolation factor f for CO_2 - H_2O - N_2 atmospheres. The curves show results for various choices of surface pressure, P , in bars. In all cases CO_2 is the major atmospheric constituent and $\text{N}_2/\text{CO}_2 = 0.03$ (b) Surface temperature of Mars as a function of surface pressure for CH_4 - NH_3 - H_2O - H_2 atmospheres of varying composition. In all cases, CH_4 is the dominant gas species. From Pollack (1979).

A portion of the polar regions of Mars consists of a layered sedimentary deposit (Cutts 1973). This laminated terrain is many layers thick, with individual layers having an approximately uniform thickness of 30 m. The layers are thought to be composed of a mixture of fine-grained dust and water ice, which were transported by winds and preferentially deposited in the polar regions. Quasi-periodically varying climatic conditions are believed to be responsible for the layered nature of this terrain (Cutts 1973, Pollack 1979). The most obvious drive for these climatic variations are the quasi-periodic changes of orbital eccentricity, axial tilt, and axial precession, which have periods of 10^5 – 10^6 years (Ward et al 1974). The amplitudes of these variations for Mars are much larger than for the Earth, with the eccentricity changing from 0 to 0.14 and the obliquity varying from 15 to 35° . Some direct evidence in favor of the astronomical climate model was provided by Pollack et al (1979b), who inferred a time scale of $\sim 10^5$ years to form a lamina from observed aerosol mass loadings and their temporal variations above the Viking lander sites.

One question connected with the astronomical theory of the laminated terrain is the mechanism for preferential aerosol deposition in the polar regions. Cutts (1973) suggested that this was due to the net downward velocity of the atmosphere during the polar winter resulting from the formation of the seasonal CO_2 polar cap. However, Pollack (1979) has pointed out that scavenging of dust and water ice by CO_2 ice in the winter polar region is probably a much more effective agent of preferential deposition. In addition, dust that migrates towards the polar region acts as a condensation center for water ice, so that in general both water and dust are contained in all the particles that settle out of the winter polar atmosphere and form the layered terrain (note that during the subsequent summer, the CO_2 ice sublimates).

A second question connected with the formation of the layered terrain is the manner in which astronomical variations lead to the building of the individual layers. Cutts emphasized the joint role of eccentricity and axial precession variations in modulating dust storm activity. This was motivated by the tendency of present-day global dust storms to occur only at times close to orbital perihelion. Perhaps an even more important factor is obliquity, whose variations can strongly modulate the atmospheric pressure (Pollack 1979). As discussed above, there may be a large reservoir of adsorbed CO_2 contained within the regolith. The bulk of this reservoir is at high latitudes. Hence, at times of high obliquity, the annually averaged polar temperatures are higher and so the atmospheric pressure increases. Calculations by Fanale & Cannon (1979) and Toon et al (1979), based on Figure 4, suggest that the atmospheric pressure varies from less than 1 mb at obliquity minimum to about 20 mb at obliquity maximum. At the

lowest pressures, global dust storms are probably impossible as supersonic wind speeds would be required, while at the highest pressures global dust storms could occur all year round (Pollack 1979). In this way, obliquity variations modulate the dust loading of the atmosphere and, hence, the dust deposition rate in the polar regions. Fanale & Cannon (1979) and Toon et al (1979) also find that permanent polar caps of CO₂ ice form at obliquity minimum, largely at the expense of the CO₂ contained in the regolith. Obliquity variations can also modulate the amount of water ice deposited in the polar regions by increasing temperatures at equatorial and middle latitudes and decreasing them in the polar regions at times of low obliquity. According to Toon et al (1979), these temperature variations cause a poleward retreat of the midlatitude boundary of subsurface permafrost and an increase in water ice deposition in the polar regions at times of low obliquity. The above discussion implies that variations in both the amount of dust and water ice deposited in the polar regions and their relative proportions occur over an obliquity cycle.

The above discussion has focused on the manner in which the polar sedimentary deposits have been built up over time. At present, there may also be a significant recycling of material within the polar laminated terrain, which is caused by the joint effects of eccentricity and axial variations acting on the water ice component (Toon et al 1979). These modulations may cause a continual migration of large scale features in the laminated terrain (Toon et al 1979).

Venus

In this subsection, we consider the reasons that the atmospheres of the Earth and Venus are so different, the question of whether Venus' surface temperature was always as high as it is today, and the compositional evolution of the atmosphere. As shown in Table 1, Venus' surface temperature is elevated by about 500 K over the effective temperature at which it radiates to space, in contrast to a modest elevation of 33 K in the case of the Earth. Related to this difference is the presence in Venus' atmosphere of the vast bulk of its outgassed volatile inventory, whereas much of the Earth's inventory is stored in near-surface reservoirs. According to the discussion of the subsection on the origin of the terrestrial atmospheres, rare gases and perhaps other volatiles were incorporated into the outer three terrestrial planets at times when the nebular temperatures were very similar in the various regions of planet formation. The similar abundances of outgassed CO₂ and N₂ for Venus and the Earth may therefore imply similar abundances of outgassed water (Pollack & Black 1979). If this is true, then the current differences in atmospheric mass and surface temperature between Venus and the Earth

cannot be due to differences in the composition of their outgassed volatiles.

The above differences between the two planets can be understood in terms of the extreme sensitivity of surface temperature to the amount of sunlight absorbed by a planet (Ingersoll 1969, Rasool & de Bergh 1970, Pollack 1971). This sensitivity arises from the control exerted by near-surface reservoirs on the amount of H_2O and CO_2 in the atmosphere, with these gas abundances depending exponentially on temperature. Since the amount of greenhouse warming depends on the amount of CO_2 and H_2O in the atmosphere, there is a strong positive feedback between surface temperature and gas amount. As illustrated in Figure 7, increasing the insolation at the top of a H_2O - N_2 atmosphere from the current value at Earth to the current value at Venus leads to a very sharp rise in surface temperature and the emplacement of all the volatiles into the atmosphere, a process termed a "runaway greenhouse" (Pollack 1971). Similar results are found when CO_2 and carbonate rocks are considered together with H_2O vapor and oceans (Rasool & de Bergh 1970).

Figure 7 also illustrates another interesting circumstance. Venus' surface may have had a moderate temperature during early epochs when the solar luminosity was considerably lower. When allowance is made for the presence of CO_2 at levels consistent with thermodynamic equilibrium

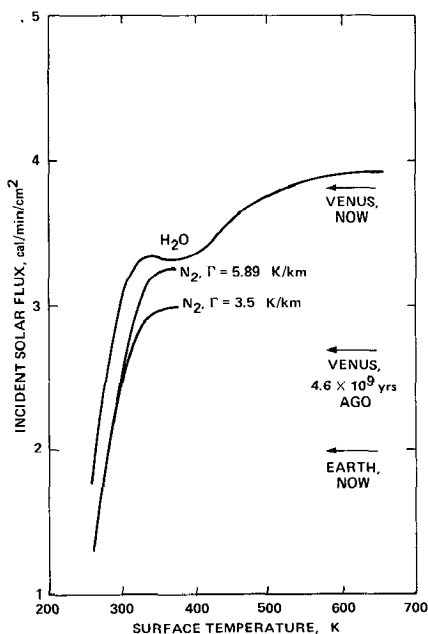


Figure 7 Surface temperature as a function of solar flux for N_2 - H_2O atmospheres having 1 bar of N_2 partial pressure. Γ is the tropospheric lapse rate. From Pollack (1971).

with carbonate rocks, this conclusion remains unaltered (Pollack 1979). Thus, the “runaway greenhouse” may not have occurred on Venus until an intermediate epoch, at a time when the solar luminosity reached a critical level. This deduction is still quite tentative since thermodynamic-equilibrium considerations are at best a crude indicator of the atmospheric CO_2 content (Walker 1977, Holland 1978a). However, if this conclusion is correct, one could further speculate that life may have arisen on Venus as it did on the Earth, but that the Venusian biota were ultimately wiped out by the rising surface temperature. Future high resolution photographs of Venus’ surface, as obtained from ground-based and spacecraft radar, might provide constraints on the planet’s early environment by, for example, finding ancient river beds.

The evolution of Venus’ atmosphere from a mildly reducing state to a fully oxidized state should have been similar to that for the Earth and so will not be repeated here. Instead, we focus on the matter of how much water vapor may have been eliminated from Venus’ atmosphere over the course of time. If Pollack & Black (1979) are correct, Venus initially may have had an amount of water with an equivalent depth of about 1 km, while today there is at most 1 m of H_2O in the atmosphere (Table 1).

When H_2O is a major atmospheric constituent, the tropopause cold trap ceases being effective and the mixing ratio of H_2O in the stratosphere is comparable to its value in the lower troposphere (Ingersoll 1969). As a result, water vapor has access to almost all the available photons that can dissociate it (Figure 3) and it is fragmented at a rate approaching 10^{13} molecules/ cm^2/s . This rate is four orders of magnitude larger than the dissociation rate of water in the Earth’s atmosphere today (Figure 3). Furthermore, the abundant H and H_2 in the uppermost atmosphere, resulting from water dissociation, elevate the exospheric temperature far above its current cold value ($\lesssim 400$ K). In this case, the rate of escape of H is not controlled by the exospheric temperature, but by either diffusion or photon limitations (Walker 1975). Since the limiting flux is proportional to the abundance of H-containing species in the stratosphere, it is much larger than for the present Earth ($\sim 10^8$ H/ cm^2/s) and is comparable to the rate at which water is photodissociated. If the escape rate of H were equal to 10^{13} atoms/ cm^2/s , an ocean of water could be lost in only 30 million years (Walker 1975).

After an initial rapid loss of water vapor from the atmosphere, the rate of loss slowed down considerably for several reasons. First, with a diminishing water vapor mixing ratio in the troposphere and an increasingly effective tropopause cold trap, the diffusion flux decreases and becomes the limiting factor (Walker 1975). Also, O_2 becomes a major atmospheric constituent and its elimination becomes the central problem,

both to prevent it from shielding H_2O too effectively from dissociating photons and from rapidly converting H and H_2 back to H_2O . Walker (1975) suggests that O_2 can be eliminated from the atmosphere by the chemical weathering of the surface. But he requires a weathering rate comparable to that for the Earth, despite a lack of liquid water to abet the erosion and to remove the already oxidized material. The basic difficulty with Walker's type of model is the need to get rid of large amounts of hydrogen and oxygen *at the same time*. Let us assume that, to first order, the escape of hydrogen is proportional to the mixing ratio of total hydrogen ($\text{H} + \text{H}_2$), f_{H} , and that the consumption of oxygen is proportional to the mixing ratio of oxygen f_{O_2} . In order to escape large amounts of hydrogen and bury equivalent amounts of oxygen we need high values for both f_{H} and f_{O_2} . Based on preliminary calculations by Yung & McElroy (1979) for the Earth's primitive atmosphere, it is found that high values for f_{H} and f_{O_2} cannot coexist in a H_2O - CO_2 atmosphere. For instance, if $f_{\text{H}} \gtrsim 10^{-3}$, then $f_{\text{O}_2} \lesssim 10^{-10}$. The exact calculations have not been performed for the evolution of the atmosphere of Venus, but it is easy to see that this is a fundamental difficulty. An interesting aspect of this model for the evolutionary loss of water is the possibility of a transient, but long-lived epoch when O_2 was a major constituent of the Venus atmosphere (Walker 1975).

Another possible sink for water arises from its vigorous recycling between the atmosphere and interior. During one cycle, water is removed from the atmosphere and water and hydrogen are added back, with the excess oxygen being taken up by the interior. The emitted hydrogen readily escapes to space. Hence, the net loss of water is equal to the oxygen consumed in the interior or equivalently the hydrogen emitted. The amount of water consumed in a given cycle could be as much as 10 % of the amount entering the interior, if the mantle lacks both metallic and ferric iron (Holland 1962). Thus, recycling of water could serve as an important loss mechanism if there is rapid and efficient recycling of atmospheric water.

Much water can also be lost to the interior in an irreversible manner. Fricker & Reynolds (1968) have pointed out that water is highly soluble in silicate melts, with the weight percentage of dissolved water increasing with increasing H_2O partial pressure. Thus, a large initial H_2O pressure might be reduced substantially as a result of H_2O dissolving in surface volcanic flows, which are not recycled back through the interior. Later flows can also remove some atmospheric water, although they would be less effective due to the lowered H_2O pressure. At moderate surface temperatures and hence low H_2O pressures, as is the case of the Earth, this process is not important.

Finally, redox reactions between H_2O and the reduced components of the early atmosphere can result in the elimination of some H_2O . Of particular interest is the oxidation of CO to CO_2 and the loss of the resulting H_2 through the exospheric escape of H . Clearly, only an amount of H_2O equal to the amount of CO can be eliminated in this manner. Depending on the oxidation state of iron in the volatile-bearing material, the released gases are characterized by a CO/CO_2 ratio ranging from $\sim 1/40$ to 4 (Holland 1962). Hence, an amount of water ranging from a few percent to almost 100 percent of the amount of CO_2 in Venus' present atmosphere could have been removed in this manner. While this mechanism is not effective in eliminating a full terrestrial amount of water, it could remove all the water present in a more modest, but still water-rich volatile inventory. However, this scenario is not the full story since a rather precise near equality of initial H_2O and CO is required to generate the rather low H_2O and CO mixing ratios of Venus' present atmosphere. We can also use the very low mixing ratio of CO in Venus' present atmosphere in comparison to its value in the released volatiles to argue that $\text{H}_2\text{O}/\text{CO}_2 \gtrsim 1/40$ in the released volatiles. Therefore, the material that formed Venus had at least 1% of the Earth's water endowment.

The possible exospheric escape of large amounts of hydrogen in the past that is hypothesized in the water photodissociation, interior recycling, and CO oxidation scenarios described above would have left a characteristic signature in the D/H ratio. Future measurements of the ratios of species such as D/H , HD/H_2 , $\text{HDO}/\text{H}_2\text{O}$, DCI/HCl , and DF/HF can provide definitive evidence bearing on these models of water loss.

Moon and Mercury

We discuss the sources of the current exospheric atmospheres of the Moon and Mercury and the possibility of early denser ones. It seems likely that the very thin atmospheres of the Moon and Mercury are derived from a combination of three sources: interior outgassing, accretion of solar wind ions, and accretion of atoms from the interstellar medium (Hodges 1975, Shemansky & Broadfoot 1977). The isotopic ratio $^{40}\text{Ar}/^{36}\text{Ar}$ in the lunar atmosphere is on the order of 10, whereas the solar value is much less than 1 (Kumar 1976). Thus, ^{40}Ar is almost entirely derived from the decay of ^{40}K in the lunar interior and its subsequent release to the surface. Using estimates of the bulk K content of the Moon, the lifetime of Ar in the lunar atmosphere and surface, and the observed atmospheric number density of ^{40}Ar , Hodges (1975) deduced a source strength for ^{40}Ar that is equivalent to the outgassing of 8% of the current interior production rate. This is a surprisingly large outgassing efficiency in view of the 800-km depth of the lunar lithosphere (Toksöz

et al 1978). Another major component of the lunar atmosphere is He. Since the helium concentration shows a distinct correlation with solar activity indices, the solar wind is thought to be a major source, although radioactive decay of ^{238}U and ^{232}Th may supply about 10% of the observed He (Hodges 1975). The solar wind may also be responsible for Ne, another major component of the lunar atmosphere, and for trace amounts of CH_4 , NH_3 , and CO_2 , with the latter being produced by chemical reactions between solar wind derived atoms on soil grains (Hoffman & Hodges 1975).

In contrast to the situation for the Moon, the solar wind usually does not reach the surface of Mercury, but is deflected at an altitude of about 1500 km by the planet's magnetic field. Nevertheless, some solar wind material is expected to be mixed into the magnetosphere (Kumar 1976). Furthermore, at times of intense solar activity, the enhanced solar wind can reach the surface directly. The H in Mercury's atmosphere is derived from a combination of solar wind protons and interstellar atoms (Shemansky & Broadfoot 1977), whereas interior outgassing and/or the solar wind represent the principal sources for the atmospheric He (Kumar 1976).

The components of the lunar atmosphere are lost chiefly by ionization, followed by solar wind sweeping (Kumar 1976). However, Jeans escape represents the chief loss mechanism for the H and He components of Mercury's atmosphere. Heavier components of Mercury's atmosphere are lost by photoionization, followed by magnetospheric convection into the solar wind (Kumar 1976).

Using upper limits on the H_2O , CO_2 , and CO abundances in Mercury's atmosphere and estimates of their lifetimes, Kumar (1976) inferred that the current outgassing rate of H_2O and CO_2 is at least four orders of magnitude lower for Mercury than the average rate for the Earth. In part, this extreme difference may be due to the great depth of Mercury's lithosphere at present (Figure 1), as well as a deficiency in Mercury's endowment of volatiles.

Our earlier discussion of thermal history models and lunar chronology indicated that extensive outgassing could be expected early in the history of the Moon and Mercury, in association with accretion, global internal differentiation, and somewhat later basaltic volcanism. Most of the outgassing probably took place during the first two of these epochs, which spanned about the first two hundred million years of lunar history and a somewhat longer period for Mercury (Figure 1). We now inquire as to whether an appreciable atmosphere might have developed then. The formal criterion for having a substantial early atmosphere, but a very

thin one at present, may be written as

$$L\Delta t/t < S < L, \quad (8)$$

where L is the assumed time-independent loss rate, S is the average outgassing rate during an intense outgassing epoch of duration Δt , and t is the planet's lifetime.

We can obtain a very crude estimate of S for the Moon. According to Pollack & Black (1979), Mars has outgassed about 2 bars of CO_2 , with an efficiency for outgassing that is about 10% of that for the Earth. Comparison of the composition of terrestrial and lunar rocks indicates that the Moon's interior is depleted by a factor of about 30 in the most volatile elements in comparison with the Earth's interior (Anders & Owen 1977). Allowing for both this depletion factor and a somewhat lower outgassing efficiency than for Mars, we estimate that the Moon outgassed about 1 mb of CO_2 . According to Equation (6), solar wind sweeping can eliminate about 3 mb of atmosphere over the age of the solar system. By analogy to the situation for Mars (McElroy 1972), a comparable amount can be lost by photochemical escape. However, an early lunar atmosphere dominated by CO_2 can be expected to have an exospheric temperature of about 400 K, by analogy to the exospheric temperature of Venus and Mars, and hence little loss of medium weight atoms occurs by thermal evaporation. The above estimates imply that as much as 6 mb of a CO_2 -dominated atmosphere can be lost over the age of the solar system. Hence, if about 1 mb of $\text{CO}_2\text{-N}_2\text{-Ar}$ has been outgassed from the Moon's interior in toto, only an exospheric atmosphere is expected at present. But if $\Delta t/t \sim 0.04$, then, according to Equation (8), it is possible that there was an early dense lunar atmosphere. Naturally, S is too poorly known to make a definitive statement on this interesting possibility.

Outgassed water on the Moon might also have had a long transient existence, but it too was eventually eliminated. Using the same reasoning as for CO_2 , we estimate that the Moon may have outgassed about 0.1 m of H_2O . Initially, most of this condensed. The removal of water vapor through photodissociation, escape of H, and crustal loss of O, was impeded by diffusion while the CO_2 atmosphere was present. Nevertheless, even in this case, by analogy to Mars, 0.1 m of water could have been eliminated in just a few times 10^8 years. Conceivably, this early atmosphere may have left clues about its existence in the form of alteration products, such as carbonates, ferric oxides, and hydroxylated minerals.

Similar considerations apply to Mercury. If the planet's magnetic field was established prior to or during the chief epochs of volatile release, conditions may have been more favorable, compared to the Moon, for

establishing a transient atmosphere, since sweeping by the solar wind would have been far less efficient. Without the field, Mercury's closer distance to the Sun may have made things less favorable. Once established, the transient atmosphere may have been dissipated through thermal evaporation of CO_2 (Belton et al 1967), photodissociation of CO_2 into CO and O and their thermal evaporation (Belton et al 1967), photochemical loss processes, and ionization and magnetospheric convection into the solar wind.

Finally, the above discussion of the rate at which an early lunar atmosphere was dissipated can be used to set limits on the contribution made by comets/asteroids to the volatile inventory of inner solar system bodies. In particular, this source could not have added more than about 6 mb of CO_2 to the Moon over the age of the solar system. This constraint is consistent with Pollack & Black's (1979) inference that the cometary/asteroid source was not the dominant source of the atmospheres of Venus, Earth, and Mars.

Titan

Titan, Saturn's largest moon, is the only satellite in the solar system with a substantial atmosphere. Here, we discuss the factors that gave rise to the atmosphere and the effect of loss processes on its gaseous composition and total mass. There is a large quantity of aerosols in Titan's atmosphere, which are optically thick at visible wavelengths, but optically thin at infrared wavelengths. Deposition of most of the sunlight in the aerosol layer results in a hot stratosphere (~ 160 K) and a cool surface (~ 80 K) (Danielson et al 1973, Jaffe et al 1979). Solar UV light and/or precipitated high energy particles from Saturn's magnetosphere act as energy sources for transforming some of the major atmospheric gases, such as methane, into more complicated compounds, ones capable of polymerizing. The polymerized material forms the source material of the aerosols (Podolak et al 1979, Hunten 1977).

As discussed in the subsection on interior sources, Titan's interior may have initially contained large quantities of water ice, ammonia hydrate, and methane clathrate. Interior and accretional heating resulted in the outgassing of H_2O , NH_3 , and CH_4 . Almost all of the outgassed material condensed on the surface, whose average temperature prior to condensation was ~ 85 K; these volatiles eventually migrated preferentially toward the colder polar regions.

Consider first the nature of a hypothetical, very early atmosphere that contained no aerosols. At summer solstice, an ice-covered region near the summer pole achieved a peak surface temperature of ~ 75 K, with a resulting partial pressure of ~ 6 mb of methane and much lower

values for NH_3 and H_2O , where we have assumed an ice albedo of 0.8 and an axial obliquity equal to Saturn's (27°). The evaporated gas flowed rapidly to the winter polar region, where it recondensed. Thus, ~ 6 mb represents an upper limit to the mean surface pressure at the optimum season for this very early atmosphere and substantially lower values may have applied at other seasons.

A key factor in the evolution of Titan's atmosphere from the incipient state described above to its present state was the development of an optically thick aerosol layer, resulting from solar UV/high energy particle induced chemical transformations. Since the aerosols are highly absorbing and their optical depth in the visible is at least 5 at present (Rages & Pollack 1979), it is likely that thermal radiation from the aerosols totally dominates the energy input to the surface. In this case, the average surface temperature is simply equal to $T_e/\sqrt[4]{2} \cong 73$ K, where T_e is the effective temperature. Furthermore, latitudinal and seasonal temperature variations in the atmosphere and over the surface are almost entirely eliminated, since the dynamical time scale for an air parcel to travel from the equator to the pole is short compared to the aerosol layer's radiative cooling time scale (Leovy & Pollack 1973). Thus, the partial pressure of methane in the atmosphere assumes a seasonably independent value of about 4 mb, as dictated by vapor pressure equilibrium at 73 K.

While the above end state represents an approximately time-invariant state, some modulation of the atmosphere's characteristics can be expected, due to variations in the input of energy that converts gases to aerosols. Lockwood & Thompson (1979) find that Titan's albedo shows a marked ($\sim 10\%$) secular variation on the time scale of a decade, with the phase of the variation correlating closely with the phase of solar activity. Pollack et al (1980) propose that these secular brightness variations are caused by solar related changes in the input of energy needed for aerosol production (e.g. UV light below $0.16 \mu\text{m}$). Such changes in input energy result in perturbations to the aerosols' characteristics (e.g. mean size) that determine the satellite's albedo. For our purposes, these solar-related changes in albedo are important because they modify the amount of visible sunlight absorbed by Titan by $\sim 2\%$ and hence change the surface temperature and methane partial pressure by ~ 0.5 K and $\sim 10\%$, respectively (Pollack et al 1980). The long term trend in the solar luminosity has effects analogous to the much shorter term variations discussed above. If the solar luminosity was 30% smaller 4.6×10^9 years ago than it is today, the solar input to Titan's atmosphere was about 30% less, the surface temperature was ~ 6 K cooler and the methane pressure was reduced by a factor of ~ 4 . In the future Titan's atmosphere will become more massive as the solar luminosity increases.

Due to gravitational sedimentation, the aerosols remain in the atmosphere for only ~ 1 year (Podolak & Bar-Nun 1979). Since it is unlikely that they can be converted back to their precursor gases at the cold surface temperature, their continued production represents a steady sink for the atmospheric gases, such as methane. On the basis of inferred properties of Titan's aerosols, their lifetime in the atmosphere, and constraints placed by the photolytic production rate of polymeric ethylene and acetylene, Podolak & Bar-Nun (1979) obtained a "conservative" value of 3.5×10^{-14} gm/cm²/s for the mass loss rate of both aerosols and methane from the atmosphere. Over the age of the solar system, there is a net loss of about 5×10^3 gm/cm² of CH₄, which corresponds to a pressure of ~ 1 bar. Thus, much more methane than currently resides in the atmosphere may have been lost over Titan's lifetime due to aerosol formation. Naturally, the methane ice buffer keeps the atmospheric pressure at a constant value. But the above estimate implies that Titan's surface has acquired an amount of CH₄, which is at least comparable to Mars' volatile inventory of C. Thus, outgassing from the interior seems to be the most likely source of Titan's atmosphere. We also see that polymerization of methane represents a significant potential effect for hypothesized early, highly reducing atmospheres of the terrestrial planets, as was discussed earlier in this section on the basis of theoretical considerations. At present, there may be a sedimentary blanket of organic polymers covering the surface of Titan to an average depth of ~ 50 m.

Photolysis of gases in Titan's atmosphere may have produced additional gaseous constituents. On the basis of the rate at which methane is being converted by solar UV radiation to unsaturated hydrocarbons (which are eventually polymerized), Hunten (1977) estimates that $\sim 9 \times 10^9$ molecules of H₂/cm²/s are being produced. Balancing this production rate against the diffusion-limited rate of H escape, he finds a mixing ratio of $\sim 5 \times 10^{-3}$ for H₂. Even somewhat larger steady-state abundances of H₂ might result from the possible presence of H₂S and PH₃ in Titan's atmosphere. The escape of large amounts of H₂, as implied by the above discussion, seems to be consistent with the detection of an emission cloud around Titan by the long wavelength channel of the UV photometer experiment aboard the Pioneer 11 spacecraft (D. Judge and R. Carlson, private communication). Potentially, photolysis of NH₃ vapor could generate huge amounts of N₂ (~ 20 bars) (Hunten 1977, Atreya et al 1978). However, the actual production of N₂ is probably much lower than this figure since the low surface temperature implies a very small partial pressure of NH₃; the aerosol layer intercepts many of the NH₃ dissociating photons; and N₂H₄, an intermediate product in the production of N₂ from NH₃, condenses at temperatures below ~ 150 K.

Io

Io, the innermost Galilean satellite of Jupiter, displays an unprecedented level of active volcanism, even by terrestrial standards (Smith et al 1979). Here we investigate the implications of Io's volcanism for the evolution of its volatile inventory. The high level of volcanic activity is thought to be caused by tidal heating due to Jupiter (Peale et al 1979). Strong tidal heating occurs, despite the satellite's synchronous rotation, as a result of Io's large orbital eccentricity, which is forced by resonant interactions with Europa and Ganymede. If this explanation is correct, Io may have experienced a comparable level of volcanic activity throughout most of its history. As a result of the tidal heating, the interior is molten, except for a thin crust, whose thickness is ~ 20 km or 1 % of the satellite's radius (Peale et al 1979).

Sulfur compounds dominate Io's current volatile inventory. SO_2 gas has been identified as a major component of Io's thin atmosphere (Peale et al 1979); SO_2 ice and solid elemental S are major constituents of its surface (Fanale et al 1977, 1979). At the same time, there are very stringent upper bounds on the amount of water, ammonia, carbon dioxide, and nitrogen ice and bound water on Io's surface (Pollack et al 1978, Pearl et al 1979). The very low values of the average atmospheric pressure, 10^{-8} – 10^{-11} bars (McElroy & Yung 1975), imply that very little N_2 or ^{40}Ar has accumulated in its atmosphere.

The mean density of Io is comparable to that of the Moon (cf Table 1). Hence, little if any ice was incorporated into its interior during satellite formation and its intrinsic volatiles may bear a crude resemblance to those of the terrestrial planets. Since S gases constitute some of the more abundant volatiles vented from terrestrial volcanoes, their association with volcanism on Io is not surprising. However, the Earth has outgassed considerably more H_2O vapor and C- and Cl-containing gases than S-containing gases and comparable amounts of N-containing gases (Walker 1977). Hence, the total dominance of S volatiles on Io is, at first glance, a puzzle. This puzzle remains even if we assume little S was incorporated into Io's core, in contrast to the situation for the Earth. Below, we explore the ability of efficient loss processes to explain the current absence of volatiles, aside from S compounds, on Io's surface and in its atmosphere.

Let us first consider the loss processes for water. Suppose that Io formed with the same fractional abundance of water as the Earth and hence outgassed ~ 100 m of water. Because of Io's greater distance from the Sun and its low surface temperature (~ 100 K), the dominant loss process for the terrestrial planets—photodissociation followed by

loss of H—may operate too slowly on Io for it to lose 100 m of water over the age of the solar system. For example, using the photodissociation time constant for water (Kumar 1976) and vapor pressure constraints on the amount of water vapor in Io's atmosphere at the average surface temperature, we find that no more than about 0.01 m of water can be lost in this way over 4.6×10^9 years. An attractive alternative mechanism arises from the partial dissociation of water into H_2 at typical silicate lava temperatures. Estimates of the current resurfacing rates on Io imply that an amount of mass equal to ~ 0.1 –10 times the total mass of Io has been extruded volcanically over its lifetime (Johnson et al 1979). If crustal material is preferentially used, then condensible, outgassed volatiles may be recycled ~ 10 –1000 times. According to Holland (1962), $H_2/H_2O \cong 0.01$ –1 in outgassed material, depending on the oxidation state of the iron in the melt. Hence, through repeated outgassing, a very large fraction of the water may have been converted to H_2 . Provided that the exospheric temperature, T_{ex} , was greater than about 200 K, as seems reasonable (McElroy & Yung 1975), Jeans escape of H_2 proceeds rapidly enough so that the escape rate would have been limited by diffusion to the exosphere. For almost any Io atmosphere, escape at the limiting flux rate proceeds very rapidly, with all but a minute amount of the volcanic H_2 being eliminated. We also note that the O liberated from H_2O in the magma chamber might have partially been used to oxidize other gases and so may have been the source of some of the O now present as SO_2 .

Much water may also have been lost through explosive volcanism. At present, volcanic plumes have been observed to attain altitudes as high as 300 km above the surface (Johnson et al 1979). Thus, while none of the volcanic ejecta has been seen to have velocities above the escape velocity and gases would adiabatically expand and cool to too low a temperature to permit Jeans escape, occasionally this material reaches exospheric altitudes and perhaps even passes through the nearby Jovian magnetosphere. At present S-containing gases probably power the explosive volcanism (Smith et al 1979). Conceivably, at earlier times, when water was abundant, it may have powered the explosive ejecta to velocities above the escape velocity, in which case much water was lost. However, such a mechanism would result in an indiscriminate loss of all materials, including S gases, and thus would not naturally result in a totally water-depleted object that still had large amounts of S volatiles. Similarly, if S was always the dominant volatile and loss occurred only through high velocity volcanic explosions, it would be very difficult to so completely eliminate such atmospheric constituents as ^{40}Ar without greatly depleting the S volatiles. In conclusion, explosive volcanism is not the only loss mechanism for volatiles, although it could be a contributing factor.

We next consider the elimination of N_2 . Again, if a terrestrial analogue is used for Io's volatile inventory, then ~ 30 mb of N_2 would be outgassed, which would remain in the atmosphere for *average* surface temperatures on Io. In order to lose this amount of N_2 in less than 4.6×10^9 years, the escape rate must be at least 3×10^7 molecules/cm²/s. This requirement probably far exceeds the rates that can be expected from the photochemical escape processes that were effective on Mars. In particular, even with CO_2 as the dominant gas species to maximize the loss rate, we estimate that the maximum photochemical loss rate of N_2 is $\sim 10^6$ molecules/cm²/s and it would most likely be much less. In order for Jeans escape to eliminate N_2 at the desired rate, T_{ex} must be greater than 1000 K, which far exceeds estimates of T_{ex} for a predominant N_2 atmosphere (McElroy & Yung 1975). A more promising possibility arises from the interaction of Io's atmosphere with Jupiter's magnetosphere. First, consider volcanic plumes. Occasionally, the material in plumes may penetrate into the magnetosphere. In this case, some of the gases are ionized through interaction with the magnetospheric plasma and are then trapped along magnetic field lines and swept away. For reasons given above in the discussion of explosive volcanism, this scenario is probably not the whole story. Second, consider gases that are continually present in the atmosphere. Elastic scattering by the high energy protons of the Jovian magnetosphere results in the ejection of gases close to the exosphere into the magnetosphere, where they are ionized and swept away. Furthermore, a buildup in the heavy ion component of the magnetosphere due to gases derived from Io sets up a positive feedback situation, with these heavy ions also ejecting gases from Io's atmosphere. Preliminary calculations of these processes indicate that they can generate substantial loss rates, ones adequate to eliminate terrestrial amounts of N_2 over Io's lifetime (J. B. Pollack & F. C. Witteborn, in preparation).

The above magnetospheric loss mechanism can equally well remove significant amounts of atmospheric ^{40}Ar and CO_2 . The current dominance of SO_2 and S as Io's major volatiles may be due in part to their volatility being lower than ^{40}Ar , N_2 , and CO_2 , which would lead to the latter's preferential occurrence in the atmosphere and hence preferential loss at earlier times. We note that both the volcanic loss mechanism for water and the magnetospheric mechanism for the other gases would eliminate them in less than 4.6×10^9 years, even had we chosen a higher initial volatile content for Io than indicated by terrestrial standards.

At the present time, S and O atoms are being transferred from Io's atmosphere into the surrounding torus at a rate of about 10^{10} atoms/cm²/s (Johnson et al 1979), perhaps by means of the magnetospheric processes described above. If this loss rate of S has been sustained over a signifi-

cant fraction of Io's lifetime, then a total of about 1×10^{27} S atoms/cm² have been lost. But this amount of S exceeds by more than two orders of magnitude the amount in Io's entire volatile inventory that would be expected by a strict analogy to the Earth's volatile inventory (Walker 1977). Hence, a much smaller fraction of S has been segregated into Io's core than into the Earth's core.

The Giant Planets

These objects are thought to possess cores made of rocky and icy materials and gaseous envelopes that have an approximately solar elemental composition, but with perhaps some enrichment of core-type material. The envelope constitutes approximately 95, 85, 20, and 15% of the mass of Jupiter, Saturn, Uranus and Neptune, respectively (Podolak & Cameron 1974, Slattery 1977). In this section, we consider the possible relationships between the evolution of these massive gaseous envelopes and the capture of these planets' irregular satellites, the composition of their regular satellites, and changes in the composition of their observable atmospheres. Irregular satellites have orbits with large eccentricities and/or inclinations and they sometimes travel in a retrograde direction around the planet.

The giant planets may have formed in one of two ways: either the core formed first and grew to a sufficient mass to permanently capture their envelopes, perhaps by inducing a hydrodynamical instability in the nearby solar nebula (Perri & Cameron 1974); or, alternatively, a local gas instability occurred within the solar nebula, resulting in the gravitational contraction of a large gaseous envelope, which subsequently accumulated a core (Bodenheimer 1974). In either case, a gaseous envelope with dimensions of a hundred to a thousand times the current planetary size was present initially for times on the order of 10^7 years; then the envelope underwent a hydrodynamical collapse to several times its present size on a time scale of years; and subsequently has slowly contracted to its present size. During this latter phase, the large intrinsic luminosity, built up by early rapid contraction, decreased by several orders of magnitude up until the present (Pollack et al 1977, Bodenheimer et al 1979).

During the earliest epochs, when the envelopes were very distended, the giant planets had very large cross sections and may have captured small solid planetesimals ($\lesssim 10$ – 100 km) through gas drag interactions (Pollack et al 1979a). In general, the orbits of the captured bodies decayed very rapidly, through continued gas drag, to the center of the planet, thus contributing to the core. However, objects captured just prior to the hydrodynamical collapse phase may have been able to remain in the

outer portions of the planet's system, thereby becoming irregular satellites.

The regular satellites may have begun to form towards the end of the hydrodynamical collapse phase, when the outermost portions of the envelope spread out into a disk (Cameron & Pollack 1976). At this time, the planet's intrinsic luminosity may have been sufficiently high, particularly in the case of Jupiter and Saturn, to inhibit the condensation of ices close to them, thereby creating a compositional gradient within their regular satellite system (Pollack & Reynolds 1974, Pollack et al 1977). Conceivably, the systematic decrease of the mean density of the Galilean satellites with increasing distance from Jupiter was created in this way. Note that ices constitute a significant fraction of the interior of many satellites of the outer solar system. By way of contrast, ices were probably not incorporated into bodies in the inner solar system and atmosphere-forming volatiles represent only a very small fraction of their total mass.

During most of their history, the envelopes have undergone a progressive cooling. When the interior temperatures became sufficiently low, chemical constituents of the envelope may have begun to become immiscible and started to separate. A particularly interesting possibility in this regard is the immiscibility of helium in metallic hydrogen when the temperature falls below $\sim 10^4$ K (Stevenson & Salpeter 1976). Metallic hydrogen zones occur at interior pressures above several megabars. The temperatures inside Saturn may have reached this threshold, in which case some He within the metallic hydrogen zone has sunk towards the planet's center (Pollack et al 1977). Through mixing, the He depletion of the metallic zone may also lead to a helium depletion in the observable atmosphere. The gravitational energy released by the separation of He may be providing a significant fraction of Saturn's intrinsic luminosity at the present time (Pollack et al 1977). The envelopes of Uranus and Neptune are probably too small to have metallic H zones.

CONCLUSIONS

The dominant source of the atmospheres of Earth, Venus, Mars, Io, and Titan appears to be the release of intrinsic volatiles. Due to substantial heating during accretion and global internal differentiation in the case of the terrestrial planets and perhaps Titan and by tidal forces in the case of Io, most of the juvenile gases were vented into the atmosphere during the first 10^8 – 10^9 years. Additional outgassing of juvenile volatiles may have occurred episodically at later times in association with volcanic

and tectonic events. The Earth and Venus have outgassed a significant fraction of their initial endowment of volatiles, while Mars may have outgassed no more than about 20% of its endowment, due to its smaller mass. Since most volatiles were probably incorporated into planet-forming material at very similar temperatures for the outer three terrestrial planets the relative proportion of volatiles should be quite similar, with the dominant outgassed volatiles being H_2O (and associated H_2) and C-, Cl-, N-, and S-containing gases, in approximate order of abundance. However, the Moon and Mercury were apparently endowed with a much smaller fractional amount of volatiles.

Io's juvenile volatiles may have had a similar composition to those of the terrestrial planets, although the S-gas species abundances may have been substantially higher than for the Earth. Titan's outgassed volatiles were probably dominated by H_2O , NH_3 , and CH_4 , which were derived from ices. Although Titan represents an end-member of satellites of the outer solar system in having a substantial atmosphere, it is qualitatively similar to many of these satellites: volatiles constitute a significant fraction of Titan's mass, in contrast to the much lower fractional abundance of volatiles for inner solar system objects. Yet its low surface temperature acts to constrain severely both the mass and composition of its atmosphere.

The solar wind, interior outgassing of radiogenic gases, and perhaps the interstellar medium constitute the dominant sources of the present exospheric atmospheres of the Moon and Mercury. However, in their early history, outgassing of modest amounts of Earth-type volatiles probably occurred and may even have led to the formation of transient atmospheres that were much more massive than their current ones. The solar nebula is the only reasonable source for the extremely massive atmospheres of the giant planets.

The early atmospheres of the Earth, Venus, Mars, and perhaps Io were at least mildly reducing. These atmospheres evolved to their current oxidized states as a result of juvenile gases being less reducing at later times, photodissociation of water followed by the escape to space of H, other photochemical processes, and, in the case of the Earth, green plant photosynthesis followed by the burial of organic matter. Indeed, photosynthesis gave rise to large amounts of free oxygen in the Earth's atmosphere. Recycling of water through its interior, dissolution of water in magmas that were not recycled, and redox reactions with CO may have enabled Venus to lose enormous quantities of water over its lifetime. The relative ease with which H can escape from the atmospheres of satellites and the terrestrial planets has prevented H_2 from ever being the dominant

constituent of these atmospheres, in contrast to the situation for the giant planets. Photochemical escape has led to the elimination of modest amounts of N and O from Mars' atmosphere over its lifetime and modest amounts of H from Venus' atmosphere in recent times.

The Moon and Mercury lack substantial atmospheres at the present time since they have outgassed volatiles at a slower rate, averaged over their lifetimes, than the rate at which these gases were lost to space. In the case of the Moon, solar wind sweeping is the dominant loss process. In the case of Mercury, solar wind sweeping is also an important loss process, but in a more indirect fashion—ionization followed by magnetospheric convection to the solar wind. Thermal evaporation is also an important loss process for the lighter constituents of Mercury's atmosphere. Elastic scattering of constituents in Io's upper atmosphere by high energy magnetospheric particles may have led to the elimination of species more volatile than SO₂ over Io's lifetime. In particular, large amounts of outgassed ⁴⁰Ar, N₂, and CO₂ may have been lost in this manner. At present, significant amounts of SO₂ are being lost by Io to its circumjovian torus, presumably chiefly as a result of this process.

Large amounts of outgassed volatiles have been lost to surface and subsurface reservoirs as a result of condensation, adsorption, and chemical weathering in the case of the Earth, Mars, Titan, and Io. Most of the Earth's water and CO₂ reside in its oceans and carbonate rocks, respectively; most of Mars' water, CO₂, and N₂ have been lost to ice, regolith, and rock reservoirs; and most of Titan's CH₄ and Io's SO₂ reside in surface and subsurface ice deposits. However, in many of the above cases, such losses are not irreversible. For all the above objects, some reservoirs, e.g. the Earth's oceans, Mars' regolith, and Titan and Io's ice deposits, act to buffer the atmospheric content of their associated volatiles. Also volatiles contained in buried sediments have been cycled through the interiors of the Earth, Io, and Venus, and eventually outgassed back into their atmospheres. In the case of Io, such recycling has occurred many times over its lifetime as a result of tidal heating and may have played a key role in eliminating H₂O through the partial dissociation of H₂O into H₂ and O₂. This process also may have helped eliminate H₂O from Venus' past atmosphere, as mentioned earlier. In the case of the Earth, recycling of volatiles may lead to a partial kinetic control on the amounts of O₂ and CO₂ in the atmosphere.

An increase in the amount of sunlight incident on an Earth-like planet from that at the Earth's distance from the Sun to that at Venus' results in a "runaway" greenhouse, due to the very strong positive feedback between surface temperature and atmospheric water and CO₂. However, conversely,

the Earth did not ice over, but had oceans and life in its early history and water flowed across the martian surface several billion years ago, despite the solar luminosity being several tens of percent lower then. The answer to these apparent paradoxes may lie in altered early atmospheres that were capable of stronger greenhouse effects. Smaller CO₂ reservoirs and hence much larger amounts of CO₂ in Mars' past atmosphere seem to offer the most promising possibility for achieving the needed greenhouse effect for that planet, while a similar solution, perhaps in conjunction with trace amounts of NH₃ at early times, may be a viable solution for the Earth. The lower solar luminosity in the past may have permitted Venus to have a moderate surface temperature and maybe even life in its early history and may have led to a reduced partial pressure of CH₄ in Titan's past atmosphere.

Quasi-periodic variations of orbital eccentricity and axial obliquity and orientation may have modulated the atmospheres and climates of the Earth and Mars on time scales of 10⁴–10⁶ years. These variations are much larger for Mars and may have led, particularly through the obliquity oscillations, to large variations in atmospheric pressure, dust storm activity, occasional presence of permanent CO₂ ice caps, and transfer of water between polar and midlatitude sinks, whose occurrence is recorded in the polar laminated terrain. These same astronomical variations appear to be important modulators of the Pleistocene succession of ice ages on the Earth.

Finally, the large dimensions of the early giant planets may have enabled them to capture core material and irregular satellites by gas drag effects. Their early high luminosity may have set up a compositional gradient among their regular satellites. Cooling of the metallic hydrogen region of Saturn may have reached a point at which He has begun to segregate from H₂, perhaps resulting in a He depletion in its observable atmosphere.

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